

# Homoleptic phenolate complexes of zirconium(IV): syntheses and structural characterization of the first six coordinate complexes

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Homoleptic phenolate complexes of zirconium,  $[\text{Na}(\text{THF})_2][\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  and  $[\text{NH}_2(\text{CH}_3)_2][\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6] \cdot 2\text{THF}$ , were synthesized and fully characterized. To our knowledge, these complexes are the first examples for homoleptic six coordinated phenolate complexes of zirconium. Anaerobic reaction of zirconium tetrachloride with six equivalents of sodium 2-chlorophenolate afforded  $[\text{Na}(\text{THF})_2][\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  in excellent isolated yields. The geometry of the  $\text{ZrO}_6$  core is octahedral with some distortion due to interactions of the sodium cations with oxygen atoms of the 2-chlorophenolate groups. The sodium cations are bound to five oxygen atoms: three to 2-chlorophenolate groups and two to THF. The coordination sphere is completed by interaction with chloride substituents of three 2-chlorophenolate ligands. A second example of a six coordinate complex of zirconium,  $[\text{NH}_2(\text{CH}_3)_2][\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6] \cdot 2\text{THF}$ , was synthesized by the reaction of zirconium tetrakis(dimethylamino) with six or four equivalents of 2-chlorophenol. The  $\text{ZrO}_6$  core adopts a distorted octahedral geometry. Distortion is caused by hydrogen bonding between the dimethylammonium cation and the oxygen atom of one 2-chlorophenolate ligand.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy revealed that  $[\text{NH}_2(\text{CH}_3)_2][\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6] \cdot 2\text{THF}$  decomposes in solution. These observations illustrate the profound influence that weaker secondary interactions to the donor atoms can have on metal coordination geometry.

## Introduction

The coordination chemistry of alcoholate and phenolate complexes of zirconium is a diverse and fascinating area of inorganic chemistry.<sup>1</sup> While the structures of a variety of dinuclear alcoholate complexes of zirconium were described,<sup>2</sup> with complexes having a structural motif similar to the anion<sup>3</sup>  $[(\{\text{CH}_3\}_2\text{CHO})_3\text{Zr}(\mu\text{-OCH}\{\text{CH}_3\}_2)_2\text{Zr}(\mu\text{-OCH}\{\text{CH}_3\}_2)_3]^-$  or the dimer<sup>4</sup>  $[(\{\text{CH}_3\}_2\text{CHOH})(\{\text{CH}_3\}_2\text{CHO})_3\text{Zr}(\mu\text{-OCH}\{\text{CH}_3\}_2)_2\text{Zr}(\mu\text{-OCH}\{\text{CH}_3\}_2)_3(\text{HOCH}\{\text{CH}_3\}_2)]$  play a dominant role, phenolate complexes of zirconium are rarer. Only recently have some heteroleptic six coordinate complexes of zirconium been fully characterized with one, two or three phenolate groups.<sup>5</sup> In addition the synthesis and characterization of zirconocene phenolate complexes have been described.<sup>6</sup>

Since six coordinate complexes of zirconium containing a  $\text{ZrO}_6$  core are observed,<sup>7</sup> we expected the same for analogous phenolate complexes. Surprisingly, we were not able to find any indication for the synthesis and crystallographic analyses of either homoleptic four- or six-coordinate phenolate complex of any of the Group 4 metals. Only the synthesis of a homoleptic tetrakisphenolate complex of zirconium was briefly mentioned, but without X-ray crystallographic information.<sup>8</sup> The closest six coordinate example is a heteroleptic dititanium complex,  $[(\text{C}_6\text{H}_5\text{O})_3(\text{C}_6\text{H}_5\text{OH})\text{Ti}(\mu\text{-OC}_6\text{H}_5)_2\text{Ti}(\text{OC}_6\text{H}_5)_3(\text{HOC}_6\text{H}_5)]$ .<sup>9</sup> Even for other transition metals six coordinate phenolate complexes are very rare.<sup>10</sup>

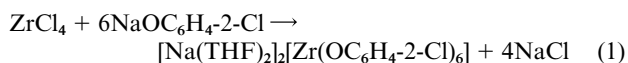
Phenolate and alcoholate complexes of zirconium have been employed in mechanistic studies<sup>2a-c,3c-g,4</sup> and as precursors for the conversion of molecular compounds to solid state materials,<sup>3g,7c,11</sup> and as co-catalysts in olefin polymerization,<sup>5e,f,6c,d,12</sup> which prompted interest in the synthesis and structural analysis of homoleptic phenolate complexes of zirconium. In general, the synthesis of monometallic species seems to be hampered by the Lewis basicity of the oxygen atom leading to aggregation *via* bridging OR groups. Only one example of a fully characterized monometallic zirconium homoleptic phenolate or alcoholate complex,  $[\text{Zr}(\text{OCH}\{\text{CF}_3\}_2)_6]^{2-}$ , is known.<sup>7c</sup> Here the formation of bridges may be hampered by the fluoride decreasing the Lewis basicity of the oxygen atom and by the presence of sodium or thallium cations.

Our goals were to establish possible strategies for the synthesis of monometallic phenolate complexes of zirconium as well as to obtain insights into the coordinative properties of these complexes. This interest is an extension of our studies on the synthesis and characterization of six coordinate thiolate complexes, wherein both monometallic and oligomeric examples were found.<sup>13</sup> We were particularly interested in the preparation of the oxygen analogs of zirconium thiophenolate complexes, which revealed an amazing diversity in their coordination geometry—varying from the octahedral to the trigonal prismatic limits.

## Results and discussion

### Synthesis and general considerations

Several methods for the synthesis of phenolate complexes of metals are known.<sup>1</sup> The first homoleptic six coordinate phenolate complex of zirconium(IV) was obtained in very good yields by treatment of zirconium tetrachloride with sodium 2-chlorophenolate in a 1 : 6 stoichiometry in tetrahydrofuran [eqn. (1)].

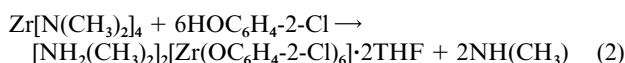


After filtration of the reaction mixture and crystallization at  $-20^\circ\text{C}$  from a mixture of hexane and tetrahydrofuran  $[\text{Na}(\text{THF})_2][\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  (**1**) was obtained as colorless crystals. Recrystallization of **1** from hexane–tetrahydrofuran afforded crystals suitable for X-ray crystallography. Complex salt **1** was soluble in acetonitrile, tetrahydrofuran and acetone and insoluble in hexane and chloroform. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra are in agreement with the structure obtained by X-ray crystallography and the chemical shifts are similar to those obtained for sodium 2-chlorophenolate and 2-chlorophenol. The UV/Vis spectrum of **1** contains three absorption bands at 212, 248 and 286 nm. Comparison with bands observed for lithium 2-chlorophenolate-tetrahydrofuran<sup>14</sup> allowed assignment of the band at 248 nm as due to tetrahydrofuran and the band at 286 nm as due to the 2-chloro-

phenolate ligands. The band at 212 nm might represent a ligand to metal charge-transfer transition.

Noteworthy, reactions of zirconium tetrachloride and lithium 2-halophenolate (halo is fluoro or chloro) in tetrahydrofuran produced intractable mixtures. Even though the  $^{19}\text{F}$ -NMR spectra of reaction solutions revealed a mixture of products, resonances assignable to lithium 2-fluorophenolate-tetrahydrofuran or to 2-fluorophenol could not be identified. The difference between the sodium and lithium phenolate reaction chemistry may be due to the strong interaction between the lithium cation and the oxygen atom of the phenolate. The interaction between the larger sodium cation and oxygen should be weaker so that the 2-chlorophenolate can act as a better nucleophile. Similar observations have been made with alkali metal enolates.<sup>15</sup> The dissociation of alkali metal enolates was found to increase with increasing atomic number of the alkali metal cation.

Another convenient method, in addition to salt elimination reactions, for the synthesis of transition metal complexes are condensation reactions of dialkylamide compounds of metals with protic compounds such as alcohols or thiols.<sup>16</sup> For example, zirconium tetrakis(*tert*-butanolate) was prepared by reaction of zirconium tetrakis(dimethylamino)<sup>17</sup> with an excess of *tert*-butanol. Similarly, alcoholysis of zirconium tetrakis(dimethylamino) using 2-propanol leads to the formation of a dimeric zirconium complex.<sup>4b</sup> In our hands, treating zirconium tetrakis(dimethylamino) with six equivalents of 2-chlorophenol in THF afforded an exothermic reaction with elimination of amine, the odor of which could be detected on changing the septum. Dilution of the reaction mixture with hexane, and storing the solution at  $-20^\circ\text{C}$ , resulted in the formation of a crystalline material identified as  $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6] \cdot 2\text{THF}$  (**2**) in good yields [eqn. (2)].



Surprisingly, 2-chlorophenol gave a six coordinate condensation product with zirconium tetrakis(dimethylamino), which contrasts the four coordinate complex obtained with *tert*-butanol and the dimer formed with 2-propanol. Attempts to prepare a four coordinate 2-chlorophenolate complex of zirconium by treating zirconium tetrakis(dimethylamino) with 2-chlorophenol in a 1 : 4 stoichiometry resulted in a 17% isolated yield of colorless crystals of **2** after crystallization from a hexane-THF mixture. The infrared spectrum of a crystalline sample of **2** contains bands in agreement with the X-ray crystal structure.<sup>18</sup> The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, however, do not agree with the structure obtained by X-ray crystallography. These NMR studies suggest that dissolving single crystals of **2** in chloroform affords at least two compounds in an approximate 1 : 10 ratio. While a single broad resonance assigned to a N-H functional group of **2** was observed more than one signal, assigned to N-CH<sub>3</sub> groups, was identified. Similar behavior is observed in the aromatic region; in addition to the four expected multiplets of the ABCDX spin system of **2** the spectrum contains further resonances of lower intensity. COSY- and HECTOR-NMR experiments reveal that the more intense peaks and the additional peaks in the aromatic region form two independent spin-systems. There is a strong solvent dependence on the ratio of the compounds in solution; crystals of **2** dissolved in acetone-*d*<sub>6</sub> show an approximate 1 : 1 ratio of the different compounds. Interpretation of a solid state  $^{13}\text{C}$ -NMR spectrum suggests the crystallized material may contain a single compound. Tentatively, these results indicate that on dissolution **2** decomposes. Similar results have been observed for other complexes containing a dialkylammonium cation.<sup>19</sup>

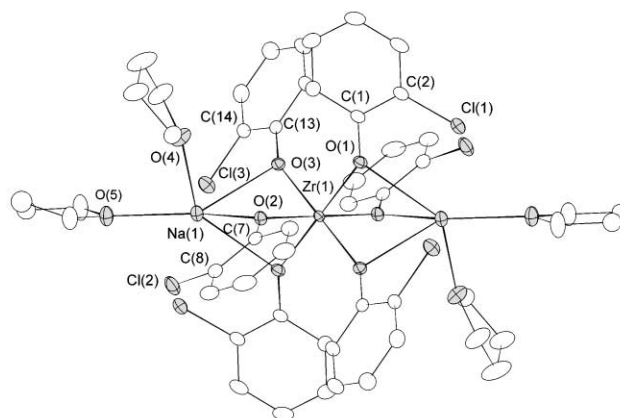
It is interesting to note that monometallic six coordinate complexes of zirconium are obtained on treating zirconium

tetrakis(dimethylamino) with the acidic 2-chlorophenol ( $\text{p}K_a = 8.25$ )<sup>20</sup> while less acidic alcohols, such as *tert*-butanol and 2-propanol ( $\text{p}K_a \approx 18$ ),<sup>21</sup> provide other types of complexes. Another example, wherein an increased acidity of a phenol derivative plays an important role, is found in the reactivity of zirconium acetylacetonate with phenols.<sup>22</sup> In the present case, the increased acidity should allow a more facile acid-base reaction between unreacted 2-chlorophenol and dimethylamine leading to the *in-situ* formation of dimethylammonium 2-chlorophenolate. Nucleophilic attack of the phenolate ion on an intermediate coordinatively unsaturated four coordinate phenolate complex of zirconium could produce the six coordinate complex.

### Crystal structures of **1** and **2**

Structural analysis of **1** and **2** by X-ray crystallography reveals the presence of anionic 2-chlorophenolate complexes of zirconium with interactions of the oxygen atoms to the cations (**1**:  $[\text{Na}(\text{THF})_2]^+$ ; **2**:  $[\text{NH}_2(\text{CH}_3)_2]^+$ ). Both **1** and **2** consist of a zirconium atom solely coordinated by the oxygen atoms of six 2-chlorophenolate ligands. As such **1** and **2** provide the only examples of phenolate complexes containing a  $\text{ZrO}_6$  core. Bond distances and angles within the 2-chlorophenolate-ligands are very similar and are not unusual.

**Structure of  $[\text{Na}(\text{THF})_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  (**1**).** Recrystallization of **1** from a mixture of THF and hexane (1 : 1) provides colorless crystals suitable for X-ray crystallography. Complex salt **1** crystallized in the triclinic space group  $P\bar{1}$ , wherein the central zirconium atom resides on a crystallographic inversion center. Fig. 1 contains the molecular structure of **1** along with a



**Fig. 1** Labeling scheme of  $[\text{Na}(\text{THF})_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$ . For clarity the hydrogen atoms have been removed.

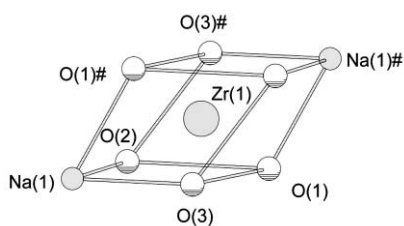
partial numbering scheme. All Zr-O bond lengths are similar with values ranging from 2.048(1) to 2.079(1) Å (Table 1). The  $\text{ZrO}_6$  core is slightly distorted from an octahedral geometry with a modest elongation along the pseudo- $C_3$  axis defined by the  $\text{Na} \cdots \text{Zr} \cdots \text{Na}$  vector. The complex has twist angles, along this axis, of  $58.86$  to  $61.02^\circ$  and *trans*-O-Zr-O bond angles of  $180^\circ$ , values close to those expected for the octahedral geometry. The sodium cations cap two opposing triangular faces of the  $\text{ZrO}_6$  core and thereby provide a skew-cuboid  $\text{O}_6\text{Na}_2$  polyhedron (Scheme 1).

Attractions of each sodium cation with three oxygen atoms [ $\text{Na}(1)\text{-O}(1)\#$ , 2.694(2);  $\text{Na}(1)\text{-O}(2)$ , 2.470(1);  $\text{Na}(1)\text{-O}(3)$ , 2.598(2)] lead to some deviations from the ideal octahedral *cis*-O-Zr-O bond angle of  $90^\circ$ . In general the O-Zr-O bond angles pointing towards the sodium cation are smaller than the other angles. For the smaller bond angles the values range between  $85.70(5)$  and  $88.12(5)^\circ$  and for the larger angles between  $91.88(5)$  and  $94.30(5)^\circ$ .

**Table 1** Selected distances (Å) and angles (°) for  $[\text{Na}(\text{THF})_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  (**1**)

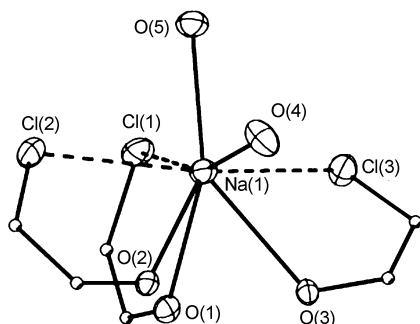
Zr(1) $\cdots$ Na(1)#	3.263(1)	Na(1)–O(1)#	2.694(2)
Zr(1) $\cdots$ Na(1)	3.263(1)	Na(1)–O(2)	2.470(1)
Zr(1)–O(1)	2.079(1)	Na(1)–O(3)	2.598(2)
Zr(1)–O(1)#	2.079(1)	Na(1)–O(4)	2.335(2)
Zr(1)–O(2)	2.075(1)	Na(1)–O(5)	2.413(1)
Zr(1)–O(2)#	2.075(1)	Cl(1)–Na(1)	3.032(1)
Zr(1)–O(3)	2.048(1)	Cl(2)–Na(1)	2.883(1)
Zr(1)–O(3)#	2.048(1)	Cl(3)–Na(1)	2.945(1)
O(1)#–Zr(1)–O(1)	180.0	O(3)–Zr(1)–O(3)#	180.0
O(1)#–Zr(1)–O(2)#	94.24(5)	Na(1) $\cdots$ Zr(1) $\cdots$ Na(1)#	180.0
O(1)–Zr(1)–O(2)	94.24(5)	Na(1) $\cdots$ Zr(1)–O(1)	124.66(4)
O(1)–Zr(1)–O(2)#	85.76(5)	Na(1) $\cdots$ Zr(1)–O(1)#	55.34(4)
O(1)#–Zr(1)–O(3)#	94.30(5)	Na(1)# $\cdots$ Zr(1)–O(1)#	124.66(4)
O(1)–Zr(1)–O(3)#	85.70(5)	Na(1)# $\cdots$ Zr(1)–O(2)#	49.16(4)
O(1)–Zr(1)–O(3)	94.30(5)	Na(1) $\cdots$ Zr(1)–O(2)#	130.84(4)
O(2)–Zr(1)–O(1)#	85.76(5)	Na(1) $\cdots$ Zr(1)–O(2)	49.16(4)
O(2)–Zr(1)–O(2)#	180.0	Na(1) $\cdots$ Zr(1)–O(3)	52.73(4)
O(2)–Zr(1)–O(3)#	91.88(5)	Na(1)# $\cdots$ Zr(1)–O(3)#	52.73(4)
O(2)#–Zr(1)–O(3)#	88.12(5)	Na(1) $\cdots$ Zr(1)–O(3)#	127.27(4)
O(2)–Zr(1)–O(3)	88.12(5)	O(1)–Zr(1) $\cdots$ Na(1)#	55.34(4)
O(3)–Zr(1)–O(1)#	85.70(5)	O(2)–Zr(1) $\cdots$ Na(1)#	130.84(4)
O(3)–Zr(1)–O(2)#	91.88(5)	O(3)–Zr(1) $\cdots$ Na(1)#	127.27(4)

Symmetry transformations used to generate equivalent atoms: #  $-x, -y, -z + 1$ .

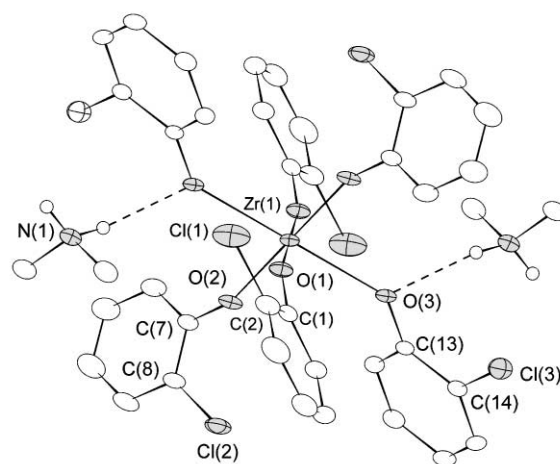
**Scheme 1**

The coordination sphere of the sodium in the two  $[\text{Na}(\text{THF})_2]$ -cations of complex salt **1** is quite interesting. Each sodium cation binds, in addition to the three oxygen atoms of three 2-chlorophenolate ligands, two oxygen atoms of THF molecules. Additionally, chlorine atoms of three 2-chlorophenolate ligands interact with the sodium cation, such that the 2-chlorophenolate acts as a chelating ligand with respect to the sodium cation, expanding its coordination number to eight. Distances between the sodium cation and the chlorine atoms range from 2.883(1) to 3.032(1) Å, which are shorter than the sum of the van der Waals radii of 3.12 Å suggesting weak interaction. Similar bonding of a sodium cation to fluoride atoms was reported<sup>7c</sup> in the complex  $[\text{Na}(\text{C}_6\text{H}_6)_2]_2[\text{Zr}(\text{OCH}(\text{CF}_3)_2)_6]$ . For this six coordinated alcoholate complex of zirconium Na–F distances of 2.675(3) and 2.810(3) Å were determined and sodium–fluorine bonding postulated (Scheme 2).

**Structure of  $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6] \cdot 2\text{THF}$  (**2**).** Recrystallization of **2** from a mixture of THF and hexane (1 : 2.5)

**Scheme 2**

provides colorless crystals suitable for X-ray crystallography. The solvated complex salt **2** crystallized in the monoclinic space group  $P2_1/n$ , with the center of the anion located on a crystallographic inversion center. Fig. 2 shows the complex salt of **2**

**Fig. 2** Labeling scheme of  $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6] \cdot 2\text{THF}$ . For clarity most of the hydrogen atoms and the THF have been removed.

along with a partial numbering scheme. The  $\text{ZrO}_6$  core is slightly distorted from an octahedral geometry by an elongation along the O(3)–Zr–O(3)# axis: Zr–O(1), 2.026(2); Zr–O(2), 1.897(2); Zr–O(3), 2.350(2) Å (Table 2). This distortion is induced by the presence of hydrogen bonding between the dimethylammonium cation and O(3) leading to elongation of the Zr–O(3) distance. Expected values for the octahedral geometry can be found in the twist angles of 57.9° and the *trans*-O–Zr–O bond angles of 180°, while deviations from ideality can be seen in the tilting of the plane defined by Zr, O(1) and O(2) of *circa* 7° relative to the axis O(3)–Zr–O(3)#. Concomitantly, *cis*-O–Zr–O bond angles deviate from 90°, wherein the angles exist in two sets: one set of small angles ranging from 81.61(7) to 85.80(7)°; and a set of larger angles ranging from 94.20(7) to 98.39(7)°.

The hydrogen atoms of the *N,N*-dimethylammonium cation form hydrogen bonds to the oxygen atoms of a tetrahydrofuran molecule and to an oxygen of a 2-chlorophenolate group: H(1A)  $\cdots$  O(3)#, 2.08(4), H(1B)  $\cdots$  O(4), 2.10(4) Å; N(1)–H(1A)  $\cdots$  O(3)#, 147(1), N(1)–H(1B)  $\cdots$  O(4), 170(3)°. The

**Table 2** Selected distances (Å) and angles (°) for  $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  (**2**)

Zr(1)–O(1)	2.026(2)	Zr(1)–O(3)	2.350(2)
Zr(1)–O(1)#	2.026(2)	N(1)–H(1A)	0.85(3)
Zr(1)–O(2)	1.897(2)	N(1)–H(1B)	0.90(3)
Zr(1)–O(2)#	1.897(2)	O(3)# $\cdots$ H(1A)	2.08(4)
Zr(1)–O(3)#	2.350(2)	O(4) $\cdots$ H(1B)	2.10(4)
O(1)#–Zr(1)–O(1)	180.0	O(2)–Zr(1)–O(3)#	81.61(7)
O(1)–Zr(1)–O(2)	94.20(7)	O(2)#–Zr(1)–O(3)	81.61(7)
O(1)#–Zr(1)–O(2)#	94.20(7)	O(2)#–Zr(1)–O(3)#	98.39(7)
O(1)–Zr(1)–O(2)#	85.80(7)	O(3)–Zr(1)–O(3)#	180.0
O(1)–Zr(1)–O(3)	96.57(7)	Zr(1)–O(1)–C(1)	147.0(2)
O(1)–Zr(1)–O(3)#	83.43(7)	Zr(1)–O(2)–C(7)	152.5(2)
O(1)#–Zr(1)–O(3)	83.43(7)	Zr(1)–O(3)–C(13)	138.63(14)
O(1)#–Zr(1)–O(3)#	96.57(7)	C(19)–N(1)–C(20)	120.6(2)
O(2)–Zr(1)–O(1)#	85.80(7)	H(1A)–N(1)–H(1B)	123(3)
O(2)–Zr(1)–O(2)#	180.0	N(1)–H(1A) $\cdots$ O(3)#	147(1)
O(2)–Zr(1)–O(3)	98.39(7)	N(1)–H(1B) $\cdots$ O(4)	170(3)

Symmetry transformations used to generate equivalent atoms: #  $-x + 1, -y, -z$ .

H  $\cdots$  O distances are smaller than the sum of the van der Waals radii of 2.60 Å.<sup>23</sup>

In summary, reliable syntheses of six coordinate homoleptic phenolate complexes of zirconium have been demonstrated. Feasible synthetic methods are salt elimination reaction of sodium phenolates and zirconium tetrachloride as well as a condensation reaction between tetrakis(dimethylamino)zirconium and acidic 2-chlorophenol. To our knowledge, complexes  $[\text{Na}(\text{THF})_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  (**1**) and  $[\text{NH}_2(\text{CH}_3)_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6] \cdot 2\text{THF}$  (**2**) are the first characterized homoleptic phenolate complexes of zirconium. The  $\text{ZrO}_6$  core of both complexes adopt a slightly distorted octahedral geometry induced by interactions of the phenolate oxygen atom and the cationic portion of the complex salts. Within **1** each sodium cation possesses three Na–O interactions resulting in an elongation along the Na–Zr–Na vector while in **2** the dimethylammonium cations each have a single N–H  $\cdots$  O interaction leading to an elongation along the O(3)–Zr–O(3)# axis. The influence of an intermolecular hydrogen-bond on the coordination geometry of a transition metal complex was described for other systems containing *N,N*-dimethylamine.<sup>4b</sup> These observations demonstrate the profound influence that weaker secondary interactions to the donor atoms can have on metal coordination geometry.

## Experimental

### Chemicals and instrumentation

All experimental work was performed under an inert atmosphere using deoxygenated solvents. All reagents were newly purchased from commercial sources and used without further purification except where noted. Zirconium tetrakis(dimethylamino) was prepared by a literature method.<sup>17</sup> All solvents were procured from Fisher and distilled: diethyl ether and THF from sodium benzophenone; acetonitrile from freshly ground  $\text{CaH}_2$ ; hexane and dichloromethane from  $\text{P}_2\text{O}_5$ . Deuterated solvents were also distilled under a positive nitrogen pressure: chloroform-*d* from  $\text{P}_2\text{O}_5$  and acetone-*d*<sub>6</sub> from calcium sulfate.

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were measured on a Varian VXR-400 FT-NMR. The <sup>19</sup>F-NMR spectrum was measured on a Gemini 200 FT-NMR. For the <sup>19</sup>F-NMR a small tube containing pure  $\text{CCl}_3\text{F}$  was inserted into the NMR tube with the sample. The signals were referenced to  $\text{CCl}_3\text{F}$  ( $\delta_{\text{F}} = 0.00$  ppm). Infrared data were collected on a Nicolet 5DXB FT-IT spectrometer. Ultraviolet–VIS spectra were recorded on a Hewlett Packard 8452 diode array spectrophotometer using Wilmad quartz spectrometer cells with a 10 mm pathlength. Elemental analyses were carried out with a Perkin-Elmer CHN Elemental Analyzer 2400. Melting points were recorded on a Thomas–Hoover capillary melting point apparatus.

Crystal data were collected with a Siemens Smart platform diffractometer [graphite-monochromated, (Mo-K $\alpha$  = 0.071073 nm; Table 3). A single crystal of each compound was selected from Paratone N oil and mounted on a 0.1 mm glass capillary. X-Ray diffraction data were collected using several different  $\phi$  settings, corresponding to a nominal hemisphere or sphere, in 0.3° increment  $\omega$ -scans. All crystals were measured at 150 K using an Oxford Cryostream 600 low temperature device. Correction for absorption and decay were applied using SADABS.<sup>24</sup> All calculations were performed on an Indigo2/Silicon Graphics Computer using SHELXS-86<sup>25</sup> and SHELXL-98.<sup>26</sup> All unique reflections were used for the refinement by full matrix least squares on  $F^2$ . The positions of all hydrogen atoms were calculated with appropriate occupancies.

CCDC reference numbers 185537 and 185538.

See <http://www.rsc.org/suppdata/dt/b2/b207299h/> for crystallographic data in CIF or other electronic format.

### Synthesis

**Preparation of  $[\text{Na}][\text{OC}_6\text{H}_4\text{-2-Cl}]$ .** To a solution of 2-chlorophenol (6.42 g, 50.0 mmol) in tetrahydrofuran (150 mL) were added small pieces of sodium (1.26 g, 55.0 mmol) at room temperature with immediate gas formation. The solution was stirred for one day resulting in a turbid yellowish solution. Volatiles were removed under vacuum providing a pale yellow oil. Addition of hexane (75 mL) resulted in the formation of a white precipitate. The hexane slurry was stirred for another day. The white precipitate was collected by filtration and washed with hexane ( $2 \times 25$  mL). All volatile components were removed from the solid under vacuum. Sodium 2-chlorophenolate (7.38 g, 49.0 mmol, 98% based on 2-chlorophenol) was obtained. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, 21 °C, 400 MHz, in ppm): 6.17 (m, 1H, *para* to C–ONa), 6.64 (dd, 1H, *ortho* to C–ONa), 6.82 (m, 1H, *para* to C–Cl), 7.03 (dd, 1H, *ortho* to C–Cl). <sup>13</sup>C-NMR (acetone-*d*<sub>6</sub>, 21 °C, 100 MHz, in ppm): 111.75 (*para* to C–ONa), 121.41 (*ortho* to C–ONa), 123.01/123.69 (C–Cl), 128.19 (*para* to C–Cl) 128.98 (*ortho* to C–Cl), 166.00 (C–ONa).

**Preparation of  $[\text{Na}(\text{THF})_2]_2[\text{Zr}(\text{OC}_6\text{H}_4\text{-2-Cl})_6]$  (**1**).** Zirconium tetrachloride (0.335 g, 1.4 mmol) and sodium 2-chlorophenolate (1.98 g, 13.1 mmol) were dissolved in tetrahydrofuran (40 mL) at room temperature resulting in an orange slurry. The reaction mixture was stirred for three days at room temperature providing a white fluffy precipitate. The precipitate was removed by filtration through Celite providing a golden solution. About three quarters of the solvent was removed under vacuum and hexane (20 mL) added. The obtained golden solution was put in a freezer at –20 °C. A small amount of white precipitate formed. The solution was again filtered through Celite and additional hexane (80 mL) was added. The

**Table 3** Crystal data and structure refinement for [Na(THF)<sub>2</sub>]<sub>2</sub>[Zr(OC<sub>6</sub>H<sub>4</sub>-2-Cl)<sub>6</sub>] (**1**) and [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Zr(OC<sub>6</sub>H<sub>4</sub>-2-Cl)<sub>6</sub>]·2THF (**2**)

	1	2
Empirical formula	C <sub>52</sub> H <sub>56</sub> Cl <sub>6</sub> Na <sub>2</sub> O <sub>10</sub> Zr	C <sub>48</sub> H <sub>56</sub> Cl <sub>6</sub> N <sub>2</sub> O <sub>8</sub> Zr
Formula weight	1190.87	1092.87
T/K	150(1)	193(1)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	10.8102(2)	10.604(2)
<i>b</i> /Å	12.1126(3)	13.538(3)
<i>c</i> /Å	12.2598(2)	18.379(4)
<i>a</i> <sup>o</sup>	111.212(1)	90
<i>β</i> <sup>o</sup>	109.659(1)	97.43(3)
<i>γ</i> <sup>o</sup>	96.699(1)	90
<i>V</i> /Å <sup>3</sup>	1356.35(5)	2616.3(9)
<i>Z</i>	1	2
Wavelength/Å	0.71073	0.71073
Absorption coefficient/mm <sup>-1</sup>	0.570	0.568
<i>F</i> (000)	612	1128
Reflections collected	16012	17047
Independent reflections	7139 [ <i>R</i> (int) = 0.0222]	6438 [ <i>R</i> (int) = 0.0319]
Data/restraints/parameters	7139/0/320	6438/0/303
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> 1 = 0.0353, <i>wR</i> 2 = 0.0900	<i>R</i> 1 = 0.0443, <i>wR</i> 2 = 0.1088
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0490, <i>wR</i> 2 = 0.0949	<i>R</i> 1 = 0.0707, <i>wR</i> 2 = 0.1206

solution was stored in a freezer at -20 °C. Within a few hours colorless crystals of **1** precipitated. The liquid phase was decanted and the crystalline solid washed twice with hexane (2 × 20 mL). The crystals of **1** (1.09 g, 0.92 mmol, 66% based on ZrCl<sub>4</sub>) were isolated in the dry box. Mp (hexane): decomposition at 123–125 °C to a white material and at 315–325 °C the white material decomposed to a brown oil. Anal. calc. for C<sub>52</sub>H<sub>56</sub>Cl<sub>6</sub>Na<sub>2</sub>O<sub>10</sub>Zr: C, 52.45; H, 4.74; N, 0.00. Found: C, 50.97; H, 4.21; N, 0.04%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, 400 MHz, 21 °C, in ppm): 1.78 (CH<sub>2</sub>), 3.61 (CH<sub>2</sub>-O), 6.33 (m, *para* to C-O, 6H), 6.69 (m, *para* to C-Cl, 6H), 7.00 (dd, *ortho* to C-O, 6H), 7.31 (dd, *ortho* to C-Cl, 6H). <sup>13</sup>C-NMR (acetone-*d*<sub>6</sub>, 21 °C, 100 MHz, in ppm): 26.19 (CH<sub>2</sub>), 68.09 (CH<sub>2</sub>-O), 116.85 (*para* to C-O), 123.15 (C-Cl), 124.03 (*ortho* to C-O), 127.56 (*para* to C-Cl), 128.86 (*ortho* to C-Cl), 161.14 (C-O). *v*<sub>max</sub>/cm<sup>-1</sup> (KBr): 3036 (w), 2962 (m), 2923 (w), 2854 (w), 1582 (m), 1478 (s), 1438 (m), 1407 (w), 1295 (s), 1264 (s), 1151 (w), 1095 (s), 1048 (s), 1086 (s), 928 (w), 861 (s), 801 (s), 747 (m), 663 (m), 598 (m), 521 (m). UV/Vis: λ<sub>max</sub>/nm (in CH<sub>3</sub>CN): 212, 248, 286.

A THF-hexane solution of **1** was stored at -20 °C. Colorless crystals suitable for X-ray diffraction experiments formed after two days.

**Preparation of [NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>[Zr(OC<sub>6</sub>H<sub>4</sub>-2-Cl)<sub>6</sub>]·2THF (**2**).** Zirconium tetrakis(dimethylamino) (0.803 g, 3.0 mmol) was dissolved in tetrahydrofuran (10 mL) providing a slightly green solution. An exothermic reaction occurred when a solution of 2-chlorophenol (2.31 g, 18 mmol) in tetrahydrofuran (15 mL) was added at room temperature and stirred for 23 h at room temperature. Hexane (40 mL) was added and the resulting solution stored at -20 °C for one day. A small amount of a white precipitate formed. The solution was filtered through Celite while cooling the flask to -20 °C. To this solution more hexane (75 mL) was added. Storing the solution at -20 °C resulted in the formation of colorless needles. Colorless crystals of **2** {2.55 g, 2.33 mmol, 78% based on Zr[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>} were isolated in the dry box. Mp (hexane): the white material was observed to change morphology at 55 °C and at 114 °C the white material melted. Anal. calc. for C<sub>48</sub>H<sub>56</sub>Cl<sub>6</sub>N<sub>2</sub>O<sub>8</sub>Zr: C, 52.75; H, 5.16; N, 2.56. Found: C, 51.31; H, 4.73; N, 2.79%. <sup>1</sup>H-NMR (chloroform-*d*, 400 MHz, 21 °C, in ppm): 1.85 (m, 8H, CH<sub>2</sub>O of THF), 2.43 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 2.59, 2.61, 3.74 (m, 8H, CH<sub>2</sub> of THF), 6.52 (ddd, appears as t, 6H, aromatic, *para* to COZr), 6.62 (t), 6.85 (ddd, appears as triplet, 6H, aromatic, *para* to C-Cl), 6.94 (t), 7.09 (ddd, appears as d, 6H, aromatic, *ortho* to COZr), 7.20 (d), 7.31 (ddd, appears as d, 6H, aromatic, *ortho* to C-Cl), 8.22 (s, 4H, NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>). <sup>13</sup>C-NMR (chloroform-*d*, 21 °C,

100 MHz, in ppm): 25.61 (s, CH<sub>2</sub>, THF), 31.57 (s, CH<sub>3</sub>, NCH<sub>3</sub>), 36.04, 36.14, 68.01 (s, CH<sub>2</sub>, CH<sub>2</sub>-O of THF), 118.16 (s, aromatic CH, *para* to C-O), 118.78, 121.90 (s, aromatic C, C-Cl), 122.45, 123.11 (s, aromatic CH, *ortho* to C-O), 127.69 (s, aromatic CH, *para* to C-Cl), 127.79, 128.77 (s, aromatic CH, *ortho* to C-Cl), 129.24, 158.71 (s, aromatic C, C-OZr). *v*<sub>max</sub>/cm<sup>-1</sup> (KBr): 3222 (w), 3053 (w), 2960 (w), 2744 (w), 2941 (w), 2404 (w), 1580 (s), 1472 (s), 1438 (m), 1297 (s), 1152 (w), 1121 (m), 1052 (m), 1025 (m), 932 (w), 863 (s), 751 (s), 685 (m), 596 (m), 519 (m), 446 (w).

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## References and notes

- (a) R. C. Fay, in *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty, eds., Pergamon Press, Oxford, 1987, Vol. 3, ch. 32; (b) M. H. Chisholm and I. P. Rothwell, in *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty, eds., Pergamon Press, Oxford, 1987, vol. 2, ch. 15.3.
- (a) W. J. Evans, M. A. Ansari and J. W. Ziller, *Polyhedron*, 1998, **17**, 869; (b) C. A. Zechmann, J. C. Huffman, K. Foltling and K. G. Caulton, *Inorg. Chem.*, 1998, **37**, 5856; (c) K. A. Fleeting, P. O'Brien, A. C. Jones, D. J. Otway, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1999, 2853; (d) Z. A. Starikova, E. P. Turevskaya, N. I. Kozlova, N. Ya. Turova, D. V. Berdyev and A. I. Yanovsky, *Polyhedron*, 1999, **18**, 941.
- (a) B. A. Vaartstra, J. C. Huffman, W. E. Streib and K. G. Caulton, *J. Chem. Soc., Chem. Commun.*, 1990, 1750; (b) S. Sogani, A. Singh, R. Bohra, R. C. Mehrotra and M. Nottmeyer, *J. Chem. Soc., Chem. Commun.*, 1991, 738; (c) B. A. Vaartstra, J. C. Huffman, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 3068; (d) R. Kuhlman, B. A. Vaartstra, W. E. Streib, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1993, **32**, 3068; (e) W. J. Evans, M. A. Greci, M. A. Ansari and J. W. Ziller, *J. Chem. Soc., Dalton Trans.*, 1997, 4503; (f) M. Veith, C. Mathur, S. Mathur and V. Huch, *Organometallics*, 1997, **16**, 1292; (g) K. A. Fleeting, P. O'Brien, D. J. Otway, A. J. P. White, D. J. Williams and A. C. Jones, *Inorg. Chem.*, 1999, **38**, 1432; (h) W. J. Evans, M. A. Johnston, M. A. Greci, M. A. Ansari, J. C. Brady and J. W. Ziller, *Inorg. Chem.*, 2000, **39**, 2125.
- (a) B. A. Vaartstra, W. E. Streib and K. G. Caulton, *J. Am. Chem. Soc.*, 1990, **112**, 8593; (b) B. A. Vaartstra, J. C. Huffman, P. S. Gradeff, L. G. Hubert-Pfalzgraf, J.-C. Daran, S. Parraud, K. Yunlu and K. G. Caulton, *Inorg. Chem.*, 1990, **29**, 3126.

- 5 (a) N. Kanehisa, Y. Kai, N. Kasai, H. Yasuda, Y. Nakayama, K. Takei and A. Nakamura, *Chem. Lett.*, 1990, 2167; (b) R. A. Kresinski, L. Isam, T. A. Hamor, C. J. Jones and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1991, 1835; (c) A. Caselli, L. Giannini, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1997, **16**, 5457; (d) W. J. Evans, M. A. Ansari and J. W. Ziller, *Inorg. Chem.*, 1999, **38**, 1160; (e) E. Y. Tshuva, S. Groyzman, I. Goldberg, M. Kol and Z. Goldschmidt, *Organometallics*, 2002, **21**, 662; (f) T. Toupance, S. R. Dubberley, N. H. Rees, B. R. Tyrrell and P. Mountford, *Organometallics*, 2002, **21**, 1367.
- 6 (a) W. A. Howard, T. M. Trnka and G. Parkin, *Inorg. Chem.*, 1995, **34**, 5900; (b) J. I. Amor, N. C. Burton, T. Cuenca, P. Gómez-Sal and P. Royo, *J. Organomet. Chem.*, 1995, **485**, 153; (c) T. Repo, G. Jany, M. Salo, M. Polamo and M. Leskelä, *J. Organomet. Chem.*, 1997, **541**, 363; (d) Y.-X. Chen, P.-F. Fu, C. L. Stern and T. J. Marks, *Organometallics*, 2002, **21**, 5958; (e) H.-R. H. Damrau, E. Royo, S. Obert, F. Schaper, A. Weeber and H.-H. Brintzinger, *Organometallics*, 2001, **20**, 5258.
- 7 (a) M. A. Hossain and M. B. Hursthouse, *Inorg. Chim. Acta*, 1980, **44**, L259; (b) M. A. Hossain, M. B. Hursthouse, A. Ibrahim, M. Mazid and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1989, 2347; (c) J. A. Samuels, E. B. Lobkovsky, W. E. Streib, K. Folting, J. C. Huffman, J. W. Zwanziger and K. G. Caulton, *J. Am. Chem. Soc.*, 1993, **115**, 5093; (d) J. A. Samuels, J. W. Zwanziger, E. B. Lobkovsky and K. G. Caulton, *Inorg. Chem.*, 1992, **31**, 4046; (e) M. Veith, S. Mathur, C. Mathur and V. Huch, *Organometallics*, 1998, **17**, 1044; (f) T. R. Ward, S. Duclos, B. Therrien and K. Schenk, *Organometallics*, 1998, **17**, 2490.
- 8 K. C. Malhotra, G. Mehrotra and S. C. Chaudhry, *Natl. Acad. Sci. Lett. (India)*, 1980, **3**, 21.
- 9 G. W. Svetich and A. A. Voge, *Acta. Crystallogr., Sect. B*, 1972, **28**, 1760.
- 10 (a) J. I. Davies, J. F. Gibson, A. C. Skapski, G. Wilkinson and W.-K. Wong, *Polyhedron*, 1982, **1**, 641; (b) W. C. A. Wilisch, M. J. Scott and W. H. Armstrong, *Inorg. Chem.*, 1988, **27**, 4335; (c) T. W. Coffindaffer, B. D. Steffy, I. P. Rothwell, K. Folting, J. C. Huffman and W. E. Streib, *J. Am. Chem. Soc.*, 1989, **111**, 4742; (d) W. Clegg, R. J. Errington, P. Kraxner and C. Redshaw, *J. Chem. Soc., Dalton Trans.*, 1992, 1431; (e) R. J. Cross, L. J. Farrugia, D. R. McArthur, R. D. Peacock and D. S. C. Taylor, *Inorg. Chem.*, 1999, **38**, 5698; (f) Y. Sun, M. V. Metz, C. L. Stern and T. J. Marks, *Organometallics*, 2000, **19**, 1625; (g) T. P. Vaid, O. L. Sydora, R. E. Douthwaite, P. T. Wolczanski and E. B. Lobkovsky, *Chem. Commun.*, 2001, 1300.
- 11 (a) T. J. Boyle, R. W. Schwartz, R. J. Doedens and J. W. Ziller, *Inorg. Chem.*, 1995, **34**, 1110; (b) M. Veith, S. Mathur, V. Huch and T. Decker, *Eur. J. Inorg. Chem.*, 1998, 1327; (c) D. Chakraborty, V. Chandrasekhar, M. Bhattacharjee, R. Krätzner, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 2000, **39**, 23.
- 12 (a) R. Duchateau, H. C. L. Abbenhuis, R. A. van Santen, A. Meetsma, S. K.-H. Thiele and M. F. H. van Tol, *Organometallics*, 1998, **17**, 5663; (b) A. van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter and A. G. Orpen, *J. Am. Chem. Soc.*, 1995, **117**, 3008.
- 13 (a) M. Könemann, W. Stüer, K. Kirschbaum and D. M. Giolando, *Polyhedron*, 1994, **13**, 1415; (b) W. Stüer, K. Kirschbaum and D. M. Giolando, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1981; (c) J. Wegener, K. Kirschbaum and D. M. Giolando, *J. Chem. Soc., Dalton Trans.*, 1994, 1213; (d) C. Puke, K. Kirschbaum, O. Conrad and D. M. Giolando, *Acta Crystallogr., Sect. C*, 2000, **56**, e542; (e) J. Friese, A. Krol, C. Puke, K. Kirschbaum and D. M. Giolando, *Inorg. Chem.*, 2000, **39**, 1496.
- 14 T. Rosen, K. Kirschbaum and D. M. Giolando, unpublished work.
- 15 L. M. Jackman and B. C. Lange, *Tetrahedron*, 1977, **33**, 2737.
- 16 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Svirastuva, in *Metal and Metalloid Amides*, Ellis Horwood limited, Chichester, England, 1980.
- 17 D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, 3857.
- 18 D. H. Williams and I. Fleming, in *Spectroscopic Methods in Organic Chemistry*, 3rd edn., McGraw-Hill Book Company, New York, 1980. Infrared data: 3222 cm<sup>-1</sup>, N-H stretching vibration; 3053 cm<sup>-1</sup>, aromatic C-H stretching vibration; 1580 and 1472 cm<sup>-1</sup>, ring stretching vibrations as two sharp and intense bands; 751 cm<sup>-1</sup>, bending vibrations for four adjacent aromatic C-H groups; 1297 cm<sup>-1</sup>, C-O stretching vibrations due to the 2-chlorophenolate ligand.
- 19 (a) See ref. 13b; (b) C. J. Carmalt, C. W. Dinnage, I. P. Parkin and J. W. Steed, *Inorg. Chem.*, 2000, **39**, 2693; (c) C. J. Carmalt, C. W. Dinnage, I. P. Parkin, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2000, 3500.
- 20 E. P. Serjeant, and B. Dempsey, *Ionisation constants of organic acids in aqueous solution*, Pergamon Press, New York, 1979.
- 21 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 2nd edn., Harper & Row, New York, 1981.
- 22 W. Evans, M. A. Ansari and J. W. Ziller, *Polyhedron*, 1998, **17**, 299.
- 23 The value for the sum of the van der Waals radii for hydrogen bound to nitrogen and oxygen (N-H...O) was taken from: J. E. Huheey, E. A. Keiter, and R. L. Keiter, in *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th edn., Harper Collins College Publishers, New York, 1993, p. 300.
- 24 G. M. Sheldrick, SADABS, Universität Göttingen, Göttingen, 1999.
- 25 G. M. Sheldrick, SHELXS-86, Universität Göttingen, Göttingen, 1986.
- 26 G. M. Sheldrick, SHELXS-98, Universität Göttingen, Göttingen, 1998.
- 27 Supporting information is archived in T. Rosen, Preparation and Characterization of Homoleptic Monodentate Phelolate Complexes of Zirconium(IV) and Lithium, 1999, MS thesis, The University of Toledo.