DALTON
FULL PAPER

Hydroxy carboxylate substituted oxozirconium clusters

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The oxozirconium clusters $Zr_6O_2(OPr)_{16}(OOC–C_{10}H_6O)_2(PrOH)_2$ and $Zr_{10}O_6(OH)_4(OOC–C_6H_4OH)_8(OOC–C_6H_4O)_8\cdot 6\,PrOH$ were obtained in quantitative yield, when $Zr(OPr)_4$ was reacted with a 10-fold excess of 1-hydroxy-β-naphthoic acid and salicylic acid, respectively. The naphthoate-substituted cluster has a rather open structure, the dianion of 1-hydroxy-β-naphthoic acid acting as a tetradentate ligand. The carboxylate group chelates one zirconium atom, and one oxygen of the carboxy group and the aryloxy group chelate a neighboring zirconium atom. In contrast, the structure of the salicylate-substituted cluster is highly condensed and contains the octahedral $Zr_6O_4(OH)_4$ core also found in other oxozirconium clusters. Four salicylate ligands bridge edges of the Zr_6 octahedron *via* their COO group; their phenolic OH groups do not coordinate to a metal atom. The other eight salicylate ligands are dianionic. Each of them bridges an edge of the Zr_6 octahedron *via* their COO group and additionally chelates one of the zirconium atoms condensed to the Zr_6 cluster core by their phenolate oxygen and one of the oxygen atoms of the COO group.

Substitution of part of the alkoxy groups in transition metal alkoxides, $E(OR)_n$, by anionic bidentate ligands (BL^-), such as carboxylates, β-diketonates, or sulfonates is used to moderate the reactivity of the alkoxides in sol–gel processing,[1] to introduce organic functionalities[2] or to control the size of the primary particles obtained by reaction with water.[1] BL-substituted derivatives are obtained by reacting the parent alkoxides with the corresponding acids H–BL (carboxylic acids, β-diketones, sulfonic acids, *etc.*). Oxo (hydroxo) clusters can often be isolated from the reactions of carboxylic acids, because esterification of an excess of the acid with the liberated alcohol produces water as the source of the oxo or hydroxo ligands. The sequence of reactions is shown for the cluster $Zr_6(OH)_4O_4(OOCR)_{12}$ as an example.[3]

$$Zr(OPr)_4 + 2\,RCOOH \longrightarrow Zr(OOCR)_2(OPr)_2 + 2\,PrOH$$

$$PrOH + RCOOH \longrightarrow RC(O)OPr + H_2O$$

$$6\,Zr(OOCR)_2(OPr)_2 + 8\,H_2O \longrightarrow Zr_6(OH)_4O_4(OOCR)_{12} + 12\,PrOH$$

Overall reaction:

$$6\,Zr(OPr)_4 + 20\,RCOOH \longrightarrow Zr_6(OH)_4O_4(OOCR)_{12} + 8\,RC(O)OPr + 16\,PrOH$$

The molecular oxo clusters can be considered the building blocks of amorphous organically modified non-silicate sol–gel materials, or at least good models for them. Particularly, they allow the study of fundamental structural issues, such as the coordination mode of the organic ligands, the accessibility of (functional) organic groups, or the kind and linkage of the coordination polyhedra.[4] The understanding of the structural implications of using bidentate ligands for the modification of metal alkoxides is necessary for a deliberate tailoring of the microstructure of the derived sol–gel materials.

Several oxo/hydroxo clusters have been obtained from the reaction of zirconium alkoxides with carboxylic acids. The clusters $Zr_6(OH)_4O_4(OMc)_{12}$ (OMc = methacrylate),[3] $Zr_6(OH)_4O_4(OOCR)_{12}(PrOH)$ (R = Ph, CMe=CH$_2$),[5] $[Zr_6(OH)_4O_4(acrylate)_{12}]_2$[5] and $Zr_6(OH)_8(OMe)_4(OOCCHPh_2)_{12}$[6] are highly condensed with square-antiprismatically coordinated zirconium atoms. They contain the $Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4$ cluster core (or the related core $Zr_6(\mu_3\text{-}OH)_8$ in the latter example) with μ_3-O and/or μ_3-OH groups capping the triangular faces of a Zr_6 octahedron. The Zr_6O_8 core of these clusters closely resembles the basic structural motif in tetragonal ZrO_2. Therefore, the clusters can be considered as nano-sized pieces of ZrO_2 surrounded by the organic ligands. Very similar cluster cores and coordination of the metal atoms was found in $Ce_6(OH)_4O_4(acetylacetonate)_{12}$[7] or $U_8(O/OH)_8[O_2P(OPh)_2]_{12}$,[8] for example.

With $Zr_6(OH)_4O_4(OMc)_{12}$ being a structural prototype, the different composition of the other clusters can be traced back to variations in the bonding mode of the carboxylate ligands. In $Zr_6(OH)_4O_4(OMc)_{12}$ and $[Zr_6(OH)_4O_4(acrylate)_{12}]_2$, all (meth)-acrylate ligands are bidentate, while there are one and four monodentate carboxylate ligands in $Zr_6(OH)_4O_4(OOCR)_{12}(PrOH)$ and $Zr_6(OH)_8(OMe)_4(OOCCHPh_2)_{12}$, respectively.

Less condensed structures are obtained when the BL : Zr ratio gets larger, as in $Zr_4O_2(OMc)_{12}$ with a distorted butterfly structure (7- and 8-coordinate Zr)[3] or polymeric $[Zr(OPr)(O_3SMe)_3]_\infty$ (7-coordinate Zr).[9] A dimeric hydroxo zirconium carboxylate with the same BL : Zr ratio was found in $Zr_2(\mu\text{-}OH)_2(OOCR)_6$ (R = μ_3-C[CpMo(CO)$_2$Co$_2$(CO)$_6$])[10] which contains a doubly carboxylate-bridged central Zr_2O_2 ring and two chelating carboxylate ligands per zirconium atom (8-coordinate Zr). The structure of $Zr_2(O^iPr)_4(OOCR)_4$ (R = μ_3-C[Co$_3$(CO)$_9$])[11] is similar. However, two of the chelating carboxylate ligands in the former structure are replaced by terminal propoxy ligands, which lowers the coordination number of the zirconium atoms to seven.

Although the hydrolytic stability of carboxylate ligands is sufficient in most cases, it can be improved by using hydroxy- or amino-carboxylic acids. The structure determination of $[Ti(OEt)_3(glycinate)]_2$ showed that this is due to the formation of a five-membered chelate ring by coordination of one oxygen of the carboxyl group and the α-amino group.[12] The bonding situation of α- or β-hydroxy carboxylates could be similar. However, these hydroxy groups are much more easily deprotonated than an α-amino group and therefore the coordination mode of hydroxy carboxylate ligands can be expected to be more complex.

Table 1 Selected bond lengths (pm) and angles (°) for **1**. Symmetry transformation to generate equivalent atoms: $1 - x, 2 - y, 1 - z$

Zr(1)–O(20)	190.0(4)	Zr(2)–O(50)	214.6(5)
Zr(1)–O(30)	229.7(4)	Zr(2)–O(80)	211.9(5)
Zr(1)–O(40)	207.3(4)	Zr(2)–O(90)	219.4(5)
Zr(1)–O(40A)	208.6(5)	Zr(3)–O(130)	192.2(5)
Zr(1)–O(50)	220.2(4)	Zr(3)–O(120)	194.5(6)
Zr(1)–O(101)	225.2(5)	Zr(3)–O(113)	207.6(5)
Zr(1)–O(100A)	242.0(5)	Zr(3)–O(90)	211.9(5)
Zr(2)–O(70)	194.0(4)	Zr(3)–O(80)	220.3(5)
Zr(2)–O(60)	203.1(5)	Zr(3)–O(100)	231.7(4)
Zr(2)–O(40A)	211.1(4)		
Zr(1)–O(40)–Zr(1A)	105.1(2)	Zr(2)–O(50)–Zr(1)	105.0(2)
Zr(1)–O(40)–Zr(2A)	143.9(2)	Zr(2)–O(80)–Zr(3)	107.5(2)
Zr(1)–O(40)–Zr(2)	110.5(2)	Zr(2)–O(90)–Zr(3)	107.8(2)

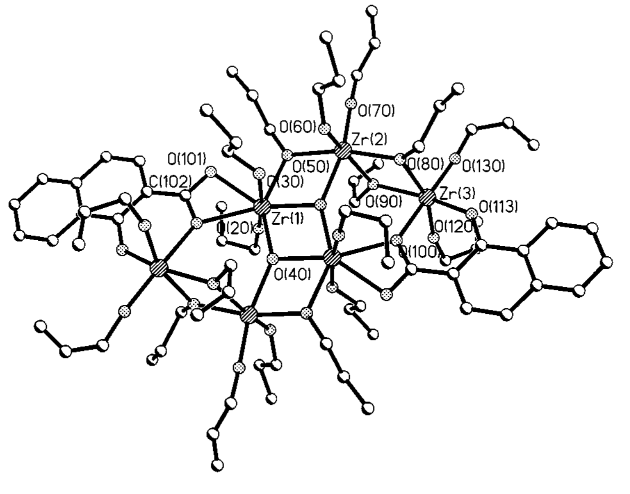

Fig. 1 The structure of $Zr_6O_2(OPr)_{16}(OOC–C_{10}H_6O)_2(PrOH)_2$ **1**. Hydrogen atoms have been omitted for clarity.

$Zr(OPr)_4$ modified by salicylate derivatives was used as precursors for zirconia based inorganic–organic hybrid materials by sol–gel processing.[1,13] Furthermore, hydroxy carboxylic acids are used in the Pechini and citrate gel methods which both allow the preparation of complex compositions with good homogeneity and control of the stoichiometry.[14] Despite this relevance to materials chemistry, no structural information is available on hydroxy carboxylate-substituted oxo clusters. Such clusters may be considered as models for the kind of building blocks in the gels formed by either method. The structures of two oxo clusters discussed in this article, obtained by the reaction of $Zr(OPr)_4$ with 1-hydroxy-β-naphthoic acid and salicylic acid as typical hydroxy carboxylic acids, thus allow the first conclusions on structural phenomena in hydroxy carboxylate modified gels to be made.

Results and discussion

When a 10-fold excess of 1-hydroxy-β-naphthoic acid ($HOOC–C_{10}H_6–OH$) was reacted with $Zr(OPr)_4$ in propanol, colorless crystals of $Zr_6O_2(OPr)_{16}(OOC–C_{10}H_6O)_2(PrOH)_2$ **1** were obtained in quantitative yield. The centrosymmetric cluster contains two μ_3-oxygen atoms, ten terminal propoxide ligands [O(20) at Zr(1), O(60) and O(70) at Zr(2), O(120) and O(130) at Zr(3), and the symmetry-related equivalents], six bridging propoxide ligands [O(50) bridging Zr(1) and Zr(2), and O(80) and O(90) bridging Zr(2) and Zr(3)], two coordinated propanol molecules and two $[OOC–C_{10}H_6O]^{2-}$ ligands.

This composition of **1** was unequivocally established by an X-ray structure analysis (Table 1, Fig. 1, 3), particularly also the fact that the naphthoate ligand is coordinated as an aryloxide carboxylate. Charge balancing then requires that two of the OPr groups must be part of coordinated propanol molecules instead of being propoxide ligands. The propanol ligands are easily identified by the Zr-O distances. While the Zr–O distances of the terminal propoxide ligands are in the range 190.0(4)-203.1(5) pm (depending on the *trans* ligands), the Zr(1)–O(30) distance is distinctly longer [229.7(4) pm] and compares well with the Zr–O distances of 226.4(3)–227.4(4) for the coordinated propanol in $Zr_6(OH)_4O_4(\text{methacrylate})_{12}(PrOH)$.[5] The Zr–O distances of the μ_3-oxygens and the bridging OPr ligands are in the same range as in the known oxo/alkoxy zirconium carboxylate clusters.

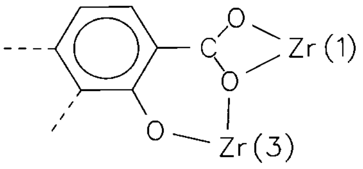

Fig. 2 Schematic drawing of the coordination of the $^{-}OOC–C_{10}H_6O^{-}$ ligands in **1**.

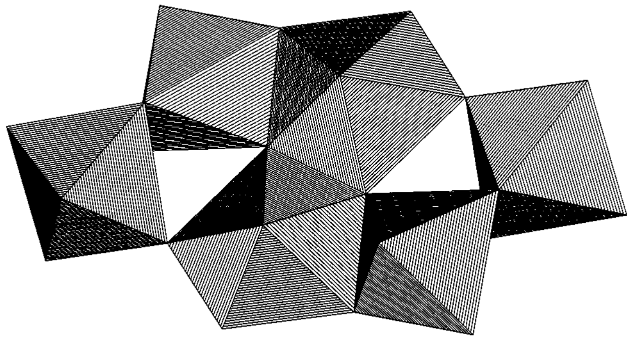

Fig. 3 The linkage of the coordination polyhedra in $Zr_6O_2(OPr)_{16}(OOC–C_{10}H_6O)_2(PrOH)_2$ **1**.

The dianion of 1-hydroxy-β-naphthoic acid acts as a tetradentate ligand. The carboxylate group chelates Zr(1), while one oxygen of the carboxyl group (O(100)) and the aryloxy group coordinate to Zr(3), thus forming a six-membered metallacycle (Fig. 2). The oxygen atom O(100) thus participates in two chelate systems at two different metal atoms and is therefore also bridging. This μ_3-bonding situation is reflected in the rather long Zr–O distances [Zr(1)–O(100) 242.0(5); Zr(3)–O(100) 231.7(4) pm]. The relatively short distance of the phenolate oxygen O(113) to Zr(3) [207.6(5) pm] is clear evidence that this is a Zr–O–R linkage. A much longer Zr–O distance would be expected for a coordinated aryl–OH group.

Four of the zirconium atoms in **1** [Zr(2), Zr(3) and their symmetry-related equivalents] are only 6-coordinate, and two [Zr(1) and Zr(1A) †] are 7-coordinate. Zr(2) and Zr(3) are linked by two bridging propoxide groups [O(80) and O(90)], *i.e.* their coordination octahedra are edge-sharing (Fig. 3). The Zr–Zr distances range from 330.1(1) to 348.5(1) pm. Zr(1) is pentagonal-bipyramidally coordinated, with the propanol ligand [O(30)] and a terminal propoxide [O(20)] in the apical positions [O(20)–Zr(1)–O(30) 172.3(2)°]. The two pentagonal bipyramids share an equatorial edge with each other and an adjacent equatorial edge with the coordination octahedron of Zr(2), the nearly planar μ_3-O(40) being common to the three coordination polyhedra. Finally, the fourth vertex of the pentagonal plane of Zr(1), occupied by the bridging oxygen atom of the carboxyl group [O(100)], links the coordination polyhedra of Zr(1) and Zr(3). Thus, the structure of the cluster $Zr_6O_2(OPr)_{16}(OOC–C_{10}H_6O)_2(PrOH)_2$ **1** is characterized by a rather open linkage of the coordination polyhedra with low coordination numbers of the zirconium atoms.

In contrast to this result, a cluster with a highly condensed core was obtained in quantitative yield when $Zr(OPr)_4$ was

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† The label 'A' refers to symmetry-equivalent atoms.

Table 2 Selected bond lengths (pm) and angles (°) for **2**. Symmetry transformation to generate equivalent atoms: $-x, y, 3/2 - z$

Zr(1)–O(11)	202.0(8)	Zr(4)–O(12)	217.5(8)
Zr(1)–O(10)	206.7(8)	Zr(4)–O(40)	234.8(8)
Zr(1)–O(82)	213.4(10)	Zr(4)–O(80)	238.1(10)
Zr(1)–O(92)	216.5(11)	Zr(4)–O(70)	266.5(10)
Zr(1)–O(32)	220.0(9)	Zr(4)–O(90)	271.4(10)
Zr(1)–O(52)	221.8(10)	Zr(5)–O(49)	195.7(10)
Zr(1)–O(12)	228.4(8)	Zr(5)–O(99)	202.4(11)
Zr(1)–O(13A)	234.2(8)	Zr(5)–O(14)	207.2(10)
Zr(2)–O(10)	203.6(9)	Zr(5)–O(90)	215.2(10)
Zr(2)–O(72)	216.1(10)	Zr(5)–O(60)	217.5(14)
Zr(2)–O(30)	223.2(10)	Zr(5)–O(22)	217.5(12)
Zr(2)–O(13)	233.8(8)	Zr(5)–O(40)	229.8(10)
Zr(3)–O(50)	218.8(10)	Zr(6)–O(89)	197.2(12)
Zr(3)–O(12)	228.4(8)	Zr(6)–O(79)	200.3(10)
Zr(3)–O(11)	202.8(8)	Zr(6)–O(14)	203.1(10)
Zr(3)–O(42)	215.9(10)	Zr(6)–O(62)	214.0(14)
Zr(4)–O(10)	203.6(9)	Zr(6)–O(70)	217.5(11)
Zr(4)–O(11A)	205.9(8)	Zr(6)–O(20)	224.9(11)
Zr(4)–O(14)	208.2(10)	Zr(6)–O(80)	230.8(11)
Zr(4)–O(13)	216.3(8)		
Zr(4)–O(10)–Zr(2)	116.6(4)	Zr(4)–O(13)–Zr(1A)	100.5(3)
Zr(4)–O(10)–Zr(1)	115.1(4)	Zr(2)–O(13)–Zr(1A)	97.8(3)
Zr(2)–O(10)–Zr(1)	118.5(4)	Zr(6)–O(14)–Zr(5)	133.3(5)
Zr(1)–O(11)–Zr(3)	118.5(4)	Zr(6)–O(14)–Zr(4)	111.9(5)
Zr(1)–O(11)–Zr(4A)	116.3(4)	Zr(5)–O(14)–Zr(4)	110.5(4)
Zr(3)–O(11)–Zr(4A)	115.1(4)	Zr(4)–O(40)–Zr(5)	94.5(3)
Zr(4)–O(12)–Zr(1)	101.8(3)	Zr(6)–O(70)–Zr(4)	88.9(4)
Zr(4)–O(12)–Zr(3)	101.4(3)	Zr(6)–O(80)–Zr(4)	93.2(4)
Zr(1)–O(12)–Zr(3)	99.2(3)	Zr(4)–O(90)–Zr(5)	88.3(4)
Zr(4)–O(13)–Zr(2)	100.6(3)		

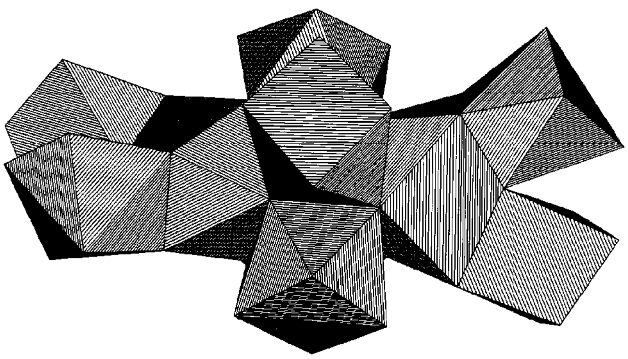

Fig. 4 The linkage of the coordination polyhedra in $Zr_{10}O_6(OH)_4(OOC–C_6H_4OH)_8(OOC–C_6H_4O)_8$ **2**.

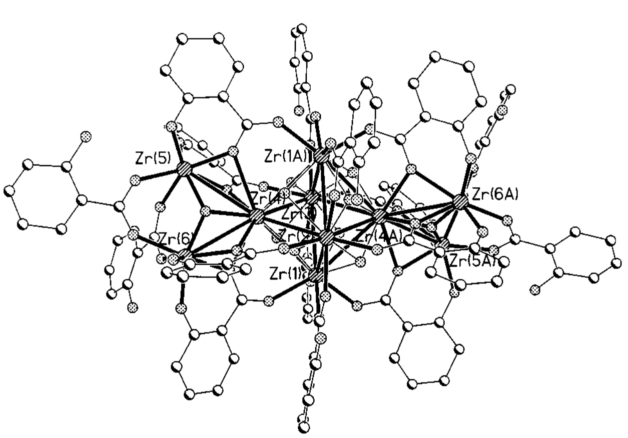

Fig. 5 The structure of $Zr_{10}O_6(OH)_4(OOC–C_6H_4OH)_8(OOC–C_6H_4O)_8$ **2**. Hydrogen atoms have been omitted for clarity.

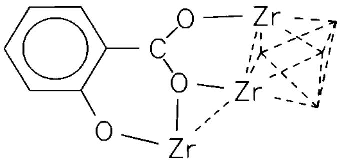

Fig. 6 Schematic drawing of the coordination of the $^{-}OOC–C_6H_4O^{-}$ ligands in **2**.

reacted with a 10-fold excess of salicylic acid in propanol under the same conditions as above (Table 2, Fig. 4, 5). The structure of $Zr_{10}O_6(OH)_4(OOC–C_6H_4OH)_8(OOC–C_6H_4O)_8 \cdot 6$ PrOH **2** is another modification of that of the prototypical cluster $Zr_6(OH)_4O_4(OMc)_{12}$,[3] where nine bridging and three chelating methacrylate ligands cover the surface of the $Zr_6O_4(OH)_4$ cluster core. The basic structural feature of **2** is again the $Zr_6(OH)_4O_4(OOCR)_{12}$ motif. In contrast to the methacrylate derivative, however, all edges of the Zr_6 octahedron are bridged by salicylate ligands. The cluster has an overall C_2 symmetry, the rotation axis passing through Zr(2) and Zr(3). The central Zr_6 unit is additionally made up of Zr(1) and Zr(4), and their symmetry-related equivalents. It is an almost undistorted octahedron, with Zr–Zr distances ranging from 345.0 to 352.6(2) pm (for comparison: Zr–Zr in $Zr_6(OH)_4O_4(OMc)_{12}$ is 348.0(2) and 354.8(4) pm). The μ_3-O and μ_3-OH units in the Zr_6 core of **2** are clearly identified by their Zr–O distances. Thus, O(10) and O(11) are the μ_3-O ligands [Zr–O 202.0–206.7(8) pm], while O(12) and O(13) are the μ_3-OH ligands [Zr–O 216.3–234.2(8) pm].

The four salicylate ligands bridging Zr(1), Zr(1A), Zr(2) and Zr(3) are in their mono-anionic form, *i.e.* the phenolic OH group is not deprotonated and does not coordinate to a metal atom. These ligands therefore are ‘normal’ bridging carboxylate ligands. The other eight salicylate ligands, *i.e.* the ligands linking Zr(1), Zr(1A), Zr(2) and Zr(3) with Zr(4) and Zr(4A), are dianionic ($^{-}OOC–C_6H_4–O^{-}$). Thus, the central cluster unit formally has the composition $[Zr_6(OH)_4O_4(OOC–C_6H_4OH)_4(OOC–C_6H_4O)_8]^{8-}$. Two $[Zr_2O(\mu\text{-}OOC–C_6H_4OH)_2]^{4+}$ units (Zr(5) and Zr(6) and their symmetry-related equivalents) are condensed to this core. Each of the doubly deprotonated salicylate ligands of the central unit acts as a bidentate ligand to either Zr(5) or Zr(6) with the phenolate oxygen and one of the oxygens of the carboxylate group as the donor atoms (Fig. 6). The interaction of Zr(5) and Zr(6) with the central unit is reinforced by the μ_3-O coordination mode of the oxide ligand [O(14)] of the condensed dimeric units.

Thus, Zr(5) and Zr(6) are 7-coordinate (two μ-OOCR, μ_3-O, two phenolate oxygens, and two bridging oxygens of the RCOO group). The Zr(4) atom of the cluster core becomes 9-coordinate by the μ_3-coordination of O(14). However, to compensate the steric crowding, the distances of Zr(4) to the bridging carboxylate oxygens are rather long [234.8(8), 238.1(8), 266.5(10) and 271.4(10); compared to 213.4–216.5 pm for the analogous distances to Zr(1)–Zr(3)].

Four of the six propanol molecules present in the crystal lattice act as proton acceptors in hydrogen bonds with the μ_3-OH groups [O(13)–O(100) 272.4 pm; O(12)–O(110) 262.3 pm]. The involvement of the μ_3-OH groups in extensive hydrogen bonding was already observed in other clusters with the $ZrO_4(OH)_4$ core[5] and shows that the acidity of these OH groups is rather high. The other two propanol molecules bridge (*via* hydrogen bonds) one of the other propanol molecules [O(120)–O(110) 269.2 pm] and the phenolic OH group of one of the salicylate ligands [O(120)–O(59) 301.3 pm].

Conclusions

Apart from the use of hydroxy carboxylic acids for the deliberate modification of sol–gel precursors, aliphatic derivatives such as lactic acid and particularly citric acid are also employed to form gels. Despite this interest, little structural information is available on hydroxy carboxylate derivatives of metal alkoxides and the derived hydrolysis products.

The structures of the two oxo zirconium clusters described in

Table 3 Summary of crystal data, data collection and structure analysis

Compound	1	2·6 PrOH
Chemical formula	$C_{76}H_{140}O_{26}Zr_6$	$C_{130}H_{124}O_{64}Zr_{10}$
Formula weight	2017.2	3622.6
Crystal size/mm	0.46 × 0.35 × 0.24	0.18 × 0.12 × 0.08
T/K	203	203
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/pm	1296.11(3)	2998.0(2)
b/pm	1315.05(3)	2150.3(1)
c/pm	1475.87(3)	2374.9(1)
α/°	75.784(1)	
β/°	76.545(1)	110.656(2)
γ/°	82.647(1)	
V ($\times 10^6$)/pm^3	2364.9(1)	14326(1)
Z	1	4
D_c/g cm^{-3}	1.415	1.651
μ(Mo-Kα)/mm^{-1}	0.703	0.791
2θ range/°	2.9–50.0	2.4–46.0
Reflections collected	7143	32918
R_{int}	0.0338	0.1117
No. independent reflections	5985	9946
No. parameters	489	870
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0528$ [5052] $wR_2 = 0.1410$	$R_1 = 0.0694$ [4175] $wR_2 = 0.1801$
Minimum, maximum Fourier-difference peaks/e Å^{-3}	0.803, −0.651	1.344, −0.782
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 11.60P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1379P)^2 + 15.93P]$ where $P = (F_o^2 + 2F_c^2)/3$

this paper therefore serve for a better understanding of how hydroxy carboxylate ligands are involved in the modification and formation of gel networks. In these examples, two coordination types are found. The first, only observed in **2**, is the 'normal' μ-coordination of the COO groups. In this bonding type, the phenolic OH group is not involved in coordination to the metal.

In the second coordination type found in both **1** and **2**, the ligands are in their aryloxide carboxylate form, *i.e.* both acidic OH groups (the carboxylic and phenolic OH group) of the parent acids were deprotonated. Despite a rather different overall composition of the clusters (**1** is alkoxide-rich with a low degree of condensation, **2** is highly condensed and alkoxide-free) the bonding mode of the aryloxide carboxylate is rather similar (see Fig. 2 and 6): the aryloxy group and one oxygen of the carboxyl group form a six-membered chelate ring with one zirconium atom, while the COO group either chelates (in **1**) or bridges (in **2**) other zirconium atoms. Thus, in contrast to other carboxylic acids used so far for the modification of zirconium alkoxides, the hydroxy carboxylic acids not only lead to a capping of coordination sites at the surface of oxo clusters, but also serve to link cluster units. This is a possible structural explanation for hydroxy carboxylic acids serving as network formers in sol–gel and related processes.

Experimental

Preparation of $Zr_6O_2(OPr)_{16}(OOC–C_{10}H_6O)_2(PrOH)_2$ 1

0.71 g of a 70% solution of $Zr(OPr)_4$ (2.11 mmol) in n-propanol was mixed under an Ar atmosphere with 10.0 g of an 11% solution of 1-hydroxy-β-naphthoic acid in propanol (21 mmol) and stored in a closed Schlenk tube at ambient temperature. A colorless crystalline solid (1.06 g) precipitated within 14 d in quantitative yield [relative to $Zr(OPr)_4$].

Preparation of $Zr_{10}O_6(OH)_4(OOC–C_6H_4OH)_8(OOC–C_6H_4O)_8$·6 PrOH 2

0.71 g of a 70% solution of $Zr(OPr)_4$ (2.1 mmol) in n-propanol was mixed under an Ar atmosphere with 10.0 g of an 11% solution of salicylic acid in propanol (21 mmol) and stored in a closed Schlenk tube at ambient temperature. A colorless crystalline solid (0.75 g) precipitated within 14 d in quantitative yield [relative to $Zr(OPr)_4$].

Structure determinations (Table 3)

Selected crystals were frozen in a droplet of perfluoropolyether and mounted on a Siemens SMART diffractometer with a CCD area detector. Graphite-monochromated Mo-Kα radiation (71.073 pm) was used for all measurements. The crystal-to-detector distance was 3.85 cm. A hemisphere of data was collected by a combination of three sets of exposures at 203 K. Each set had a different φ angle for the crystal, and each exposure took 15 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The structure was solved by direct methods (SHELXS86). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom.

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See http://www.rsc.org/suppdata/dt/1999/1301/ for crystallographic files in .cif format.

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