Coordination Chemistry Reviews 350 (2017) 61–67

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Surface chemistry of carboxylato-substituted metal oxo clusters – Model systems for nanoparticles

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ARTICLE INFO

Article history:
Available online 15 May 2017

Dedicated to Pierre Braunstein on the occasion of his 70th birthday.

Keywords:
Ligand dynamics
Cluster rearrangement
Cluster degradation
Ligand exchange
Surface functionalization
Nanostructures

ABSTRACT

Clusters can be model systems for nanoparticles with regard to the chemistry of surface groups. Metal oxo clusters with carboxylato ligands are easily accessible and therefore well-suited for investigating the chemistry of cluster-bonded ligands. This review article gives an account on issues like ligand dynamics, post-synthesis ligand exchange, stability of the cluster core during ligand exchange, possible mechanisms of intra- and intermolecular ligand exchange or utilizing functional ligands.

Contents

1. Introduction

A key issue in the chemistry of nanoparticles is their stabilization by means of suitable surface groups [1–3]. These groups not only prevent aggregation and growth of nanoparticles, but also control their shape and reactivity, interact with the environment, influence their physical properties and allow functionalization by organic groups. An understanding of the chemistry of the (mostly organic) groups attached to the nanoparticle surface is therefore of utmost importance.

Clusters can be model systems for nanoparticles with regard to the chemistry of surface groups, which can be the same as for nanoparticles of the same composition. They are called "ligands" in the remainder of this article, because their bonding characteristics and the other issues discussed here are equivalent to what is known from coordination chemistry. Investigating clusters has several advantages compared with nanoparticles. Clusters have clearly defined structures (no size distribution) and can be investigated with molecular chemistry methods. Furthermore, bonding of ligands in chemically non-equivalent positions at the cluster surface can be distinguished.

This article concentrates on titanium and zirconium oxo clusters, preferentially with carboxylato and alkoxo surface groups.

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http://dx.doi.org/10.1016/j.ccr.2017.05.002
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The cluster cores have typical diameters in the range 0.8–1.5 nm. Clusters of this type have been investigated in more detail than others, because they are easily prepared by reaction of the corresponding metal alkoxides and carboxylic acids, and many examples with different cluster cores and carboxylate ligands are known. Preparation and structures will not be discussed in this article as it was summarized elsewhere [4,5].

2. Ligand dynamics

The notion that ligands are fixed at certain positions on the cluster surface, which is implied by the common ball-and-stick representations, is very often not correct. The solution NMR spectra of many clusters only exhibit averaged signals for ligands in stereochemically different positions (*i.e.*, the ligands dynamically move on the cluster surface), while they are clearly resolved in other clusters. There is currently no general rule which structural parameters favor a dynamic or static behavior of the ligands at a given temperature. The only distinct, but somehow trivial tendency is that ligands bonded to the cluster through three oxygen atoms are rarely dynamic, in contrast to bidentate ligands. Typical examples are the phosphonato-substituted clusters $Ti_4O(OiPr)_8(O_3PR)_3(DMSO)$ [6,7] or $Ti_6O_4(OiPr)_{10}(OAc)_2(O_3PR)_2$ (OAc = acetate) [8] where the solution NMR signals of all ligands at room temperature can be clearly correlated with the crystallographically determined structure of the clusters, *i.e.*, the clusters have static structures.

Dynamic carboxylate shifts were, for example, investigated in detail for the tetranuclear Zn (and related Cd) clusters $Zn_4(OOCR)_6L_2$ (L = 1,3-bis(dimethylamino)-2-propanolate [9] and 2,6-bis(1-(2-hydroxyphenyl)-iminoethyl)pyridine [10]). The postulated mechanisms include interconversion of chelating and bridging carboxylato ligands. A metal *oxo cluster* for which this interconversion was studied in detail is $Zr_4O_2(OMc)_{12}$ (OMc = methacrylate). According to X-ray structure analyses, its idealized molecular symmetry is C_{2h}, with four non-equivalent (one chelating and three bridging) ligand positions (Fig. 1). Nevertheless, only one sharp set of OMc protons was observed in the solution 1H NMR spectrum at room temperature [11]. At −80 °C, however, sharp signals of the four non-equivalent ligands were observed, with an intensity ratio of 1:1:2:2 according to the C_{2h} symmetry of the cluster.

Four interconversion processes were identified by means of temperature-dependent EXSY spectra. The one with the lowest activation energy occurs at T >−70 °C between the chelating ligands (Fig. 1, position 1) and the bridging ligands in either position 3 or position 4, while the ligands in the other positions are not involved at this temperature. Upon raising the temperature to −60 °C, the ligands in position 3 additionally exchange with the ligands in position 2. Finally, at −50 °C, all ligands are involved in the intramolecular exchange processes.

Interestingly, a second, asymmetric isomer of $Zr_4O_2(OMc)_{12}$ was crystallographically identified [12], in which one OMc ligand in position 3 is chelating-bridging (chelating to the upper Zr atom in Fig. 1, and one carboxyl oxygen atom bridging the upper and the right Zr atom), instead of bridging. Solutions of the two isomers give identical NMR spectra, *i.e.* interconversion of bridging and chelating-bridging coordination is very fast on the NMR time scale. Intermediate chelating-bridging coordination could explain the easy transition from chelating to bridging coordination.

The studies on the Zn and Zr complexes indicate that interconversion of chelating and bridging carboxylato ligands is a process with low activation energy and might be responsible for the dynamic behavior of carboxylato-substituted oxo clusters. This is supported by an investigation of $Zr_6(OH)_4O_4(OOCR)_{12}$ clusters, which are known for various carboxylato ligands. Their solid-state structures consist of an octahedral Zr_6 core the triangular faces of which are alternatively bridged by μ_3-O and μ_3-OH groups. From simple structural considerations one would expect exclusively edge-bridging carboxylato ligands. DFT calculations confirmed indeed that such an O_h geometry is the most stable for the isolated $Zr_6(OH)_4O_4(OOCH)_{12}$ cluster [11]. In the $Zr_6(OH)_4O_4(OOCR)_{12}$ derivatives investigated by X-ray structure analyses, however, only nine carboxylato ligands bridge Zr-Zr edges while the remaining three are chelating. The three chelating ligands are arranged around one $Zr_3(\mu_3\text{-O})$ face of the Zr_6 octahedron (see the OMc derivative [12] in Fig. 2 as an example).

It should be mentioned at this point that all known clusters $Zr_6(OH)_4O_4(OOCR)_{12}$ co-crystallize with hydrogen-bonded carboxylic acid molecules. The μ_3-OH groups play an important role in the complex hydrogen bond interactions around the clusters, as they act as hydrogen donors to the CO groups of the carboxylic acids. The lower symmetry (C_3) in the crystal structures, compared with the geometry-optimized structure in the DFT calculation, is probably due to extensive hydrogen bonds to carboxylic acids. The presence of such molecules gives rise to degenerate carboxylate exchange processes (see Section 3) in solution (by which

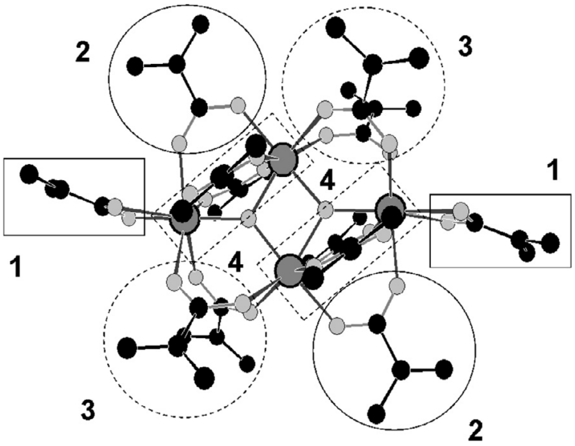

Fig. 1. Schematic presentation of the four non-equivalent ligand positions of $Zr_4O_2(OMc)_{12}$, marked with the numbers 1–4. The signal intensity in the NMR spectra of the ligands marked with broken lines is twice that of the ones marked with full lines [11].

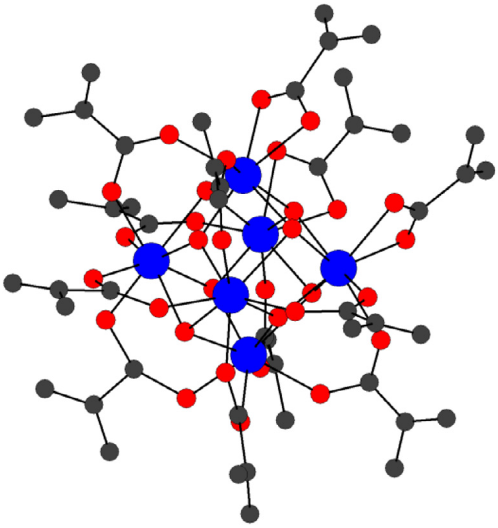

Fig. 2. Schematic presentation of the cluster $Zr_6(OH)_4O_4(OMc)_{12}$. The three chelating ligands are around the upper right Zr_3 triangle [13] (Zr: blue, O: red, C: black).

$RCOO^-$ ligands are replaced by ligands of the same kind). Complete removal of the hydrogen-bonded carboxylic acid molecules (in the solid state or in solution) is a very tedious process. Investigation of intra-cluster ligand dynamics by NMR spectroscopy, as discussed above for $Zr_4O_2(OMc)_{12}$, is therefore only possible if the clusters do not contain hydrogen-bonded carboxylic acid molecules, i.e., if there are no competing exchange processes.

Conversion between the two forms, *i.e.*, the C_3- and O_h-symmetric $Zr_6(OH)_4O_4(OOCH)_{12}$ cluster, was studied by molecular dynamics simulations, where the chelating ligands were forced to move into a bridging position in a synchronized manner [11]. One oxygen atom of each chelating carboxylate group was moved to the neighboring Zr atom, while the other was still bonded to the original Zr atom. The moving oxygen atoms were allowed to move freely perpendicular to the reaction coordinate. The energy is low at the start and the end of the forced movement (Fig. 3). However, there is a pronounced minimum in between, which corresponds to the shortest distance between the moving carboxylate oxygen and the hydrogen of the μ_3-OH group. Note that the $Zr_3(\mu_3\text{-}O)$ face of the $Zr_6O_4(OH)_4$ octahedron which is decorated by the three chelating OMc ligands is surrounded by three $Zr_3(\mu_3\text{-}OH)$ faces (Fig. 2). The dip in the energy barrier along the reaction coordinate thus comes about by formation of a hydrogen bond between the moving oxygen atom of the carboxylato ligand and a neighboring μ_3-OH group.

The examples discussed in this Section have in common that intramolecular site exchange of ligands on the cluster surface requires the concerted movement of several ligands at the same time. Dynamic behavior is favored if ligands have different coordination possibilities (e.g., terminal/bridging OR groups, chelating/bridging carboxylato ligands, etc.). The chelating-bridging ligand interconversion in $Zr_6(OH)_4O_4(OOCH)_{12}$ shows additionally that the trajectory of the motion may be more complex than anticipated and that bystander ligands may influence the movement process. The few available experimental results already indicate that the mechanisms of ligand dynamics in clusters (and analogously in nanoparticles) are more complex than analogous processes in monometallic coordination compounds. It is rather obvious that other mechanisms than the ones discussed here can also take part.

3. Post-synthesis ligand exchange

Post-synthesis exchange of one sort of ligands on the surface of a nanoparticle against another is a key tool in nanochemistry. While certain stabilizing ligands may be optimal during the preparation process, others may be more advantageous for the later use of the nanostructures. A good example is the so-called "hot-injection" method [14] by which mainly semiconductor nanoparticles can be prepared. The synthesis is performed in tri-*n*-octylphosphine oxide (TOPO) which also serves to stabilize the formed particles initially by coordination to the surface metal atoms. Before the nanoparticles can be used, however, TOPO must be exchanged against other ligands.

More relevant to the focus of this article are titania nanoparticles in the so-called Grätzel cells [15]. In these photovoltaic cells, a sensitizing dye is attached to semiconductor nanoparticles, mostly titania. To this end, the sensitizers, typically metal-organic complexes, are substituted by carboxylate groups by which they are attached to the titania nanoparticle surface. The interaction between the —COO group and titania is not only of fundamental importance in determining the geometrical structure of the adsorbed dye and influencing the electronic coupling with titania, but also for the stability of the device.

In the following, carboxylato-substituted metal oxo clusters again serve as model systems for some issues associated with post-synthesis ligand exchange. This includes among others the question of cluster rearrangement and degradation during the exchange process, exchange mechanisms, intended or unintended partial exchange of ligands or preference for specific surface sites.

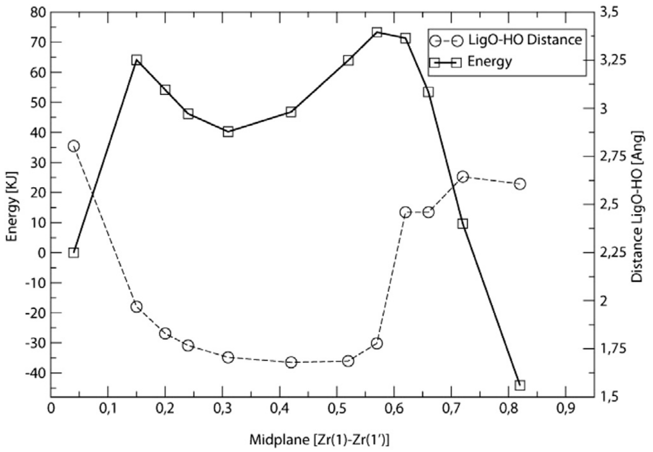

Fig. 3. Energy profile (left scale) for the synchronized ligands movement from chelating (left) to bridging positions (right). The distance between the moved carboxylate oxygen and the hydrogen of the μ_3-OH group is given on the right scale [11].

3.1. Stability of the cluster core

Metal oxo clusters are stable when both the total charge and coordination numbers of the metals are balanced by the sum of all ligands. The risk that the cluster rearranges or degrades upon ligand exchange is therefore minimized, if the leaving and entering ligands have the same charge and occupy the same number of coordination sites. Even if taking this basic rule into account, rearrangement or degradation of the cluster core has been observed for metal oxo clusters, and other criteria apparently play a role. An example are the various attempts to prepare carboxylato-substituted titanium oxo clusters by reaction of carboxylic acids with alkoxo/oxo clusters. Because the latter often contain μ_2-OR groups, replacement of μ_2-OR by bridging carboxylato ligands would neither change the total charge of the ligands nor the number of occupied coordination sites. As a matter of fact, the cluster core was essentially retained when $Ti_3O(O\textit{i}Pr)_{10}$ was reacted with benzoic acid, and $Ti_3O(O\textit{i}Pr)_8(OOCPh)_2$ was obtained [16]; the benzoate ligands were replacing μ_2-OR group. When $Ti_{16}O_{16}(OEt)_{32}$ was reacted with small proportions of carboxylic acids or acetylacetone (H-acac), a fraction of the bridging OEt groups was replaced by bridging carboxylato or acac groups. For higher carboxylate:Ti proportions, the cluster was degraded [17]. On the other hand, reaction of $Ti_7O_4(OEt)_{20}$ with benzoic acid resulted in the formation of the new cluster $Ti_6O_4(OEt)_{14}(OOCPh)_2$ with concomitant major rearrangement of the cluster core, despite the presence of μ_2-OR groups in the starting cluster [18]. The main difference between μ_2-OR and bridging carboxylato or acac ligands is the orientation of the two M-O vectors (the "bite angle" of the ligands, respectively). As has been analyzed earlier in much detail for other bidentate ligands [19], this may have strong influence on the overall structure. In the case of the mentioned Ti oxo/alkoxo clusters, replacement of μ_2-OR by bridging carboxylato or acac ligands would require a major twisting of the $[TiO_6]$ octahedra relative to each other, which apparently is not possible in every case without rearrangement or degradation of the cluster core.

A related example are the heterotungstate clusters $[SiW_{11}O_{35}(O_5Si_2R_2)]^{4-}$ [20,21] and $[\gamma\text{-}SiW_{10}O_{32}(O_5Si_2R_2)]^{4-}$ [22] which were obtained by reaction of $[SiW_{11}O_{39}]^{8-}$ or

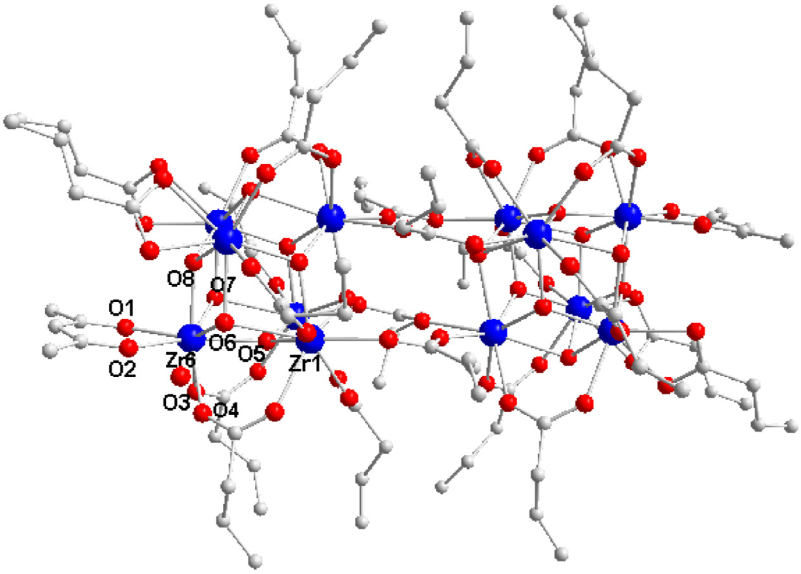

Fig. 4. Structure of (centrosymmetric) $[Zr_6O_4(OH)_4(OOCCH_2CH = CH_2)_{11}(acac)]_2$ [24] (Zr: blue, O: red). The structure consists of two Zr_6 units with very similar structures as $Zr_6O_4(OH)_4(OMc)_{12}$ discussed above. The acac ligands (bound through the atoms O1 and O2) replace one chelating OMc ligand in each half.

$[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with various $RSiX_3$ (X = Cl or OR′). In a formal sense, four surface $–O^-$ groups (formally equivalent to OH or OR) at neighboring W atoms are replaced by the bridging $R_2Si_2O_5^{4-}$ unit. Both the overall charge of the ligands and the number of occupied coordination sites is thus preserved. Furthermore, the "bite angle" of the bridging $R_2Si_2O_5^{4-}$ unit does not induce rearrangement of the clusters.

One might assume that substitution of carboxylato ligands by acac is less problematic from a structural point of view than substitution of μ_2-OR groups. But even in this case the results are diverse. The outcome of the reactions of three different carboxylato-substituted oxo clusters with acetylacetone, namely $Zr_4O_2(OMc)_{12}$ [23], $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ [24] and $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ [24], was very different. All clusters contain both chelating and bridging carboxylato ligands, and carboxylato ligands in geometrically different positions, which could have allowed accommodating acetylacetonate ligands in the most appropriate position. As a matter of fact, reaction of $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$ (R = Et, $CH_2CH = CH_2$) with acetylacetone led to site-selective substitution of up to two chelating carboxylato ligands and formation of isostructural $[Zr_6O_4(OH)_4(OOCR)_{12-x}(acac)_x]_2$ ($x \leq 1$) (Fig. 4). This is in line with the preferred chelating coordination of acac ligands to Zr. Why only one OMc ligands per Zr_6 unit was substituted is unclear. Contrary to this, reaction of $Ti_4Zr_4O_6(OBu)_4(OMc)_{16}$ resulted in detachment of two $Ti(OBu)_2(acac)_2$ units and formation of the smaller cluster $Ti_2Zr_4O_4(OMc)_{16}$. $Zr_4O_2(OMc)_{12}$ was completely degraded to $Zr(acac)_4$. The reasons for these differences are currently speculative; the robustness of the cluster core appears to play an import role. In $[Zr_6O_4(OH)_4(OOCR)_{12}]_2$, *each* metal atom of the cluster is connected to the other Zr atoms through four μ_3-O or μ_3-OH groups. Removing one or more metals from such a closed structure by a chemical reaction is apparently difficult and renders ligand substitution possible, with retention of the cluster core structure.

Exchanging one kind of carboxylato ligand against another should be least problematic taking the above-mentioned criteria into account which may influence retention of the cluster core structure during ligand exchange. This is indeed the case, and numerous post-synthesis carboxylate exchange reactions of metal oxo clusters were described, *i.e.* reactions in which cluster-bonded carboxylato ligands are exchanged by treatment with another carboxylic acid. Many of these reactions proceed also in presence of high concentrations of carboxylic acid without degradation of the cluster, but exchange may stop after partial substitution for some ligand combinations [25].

The reasons for a post-synthesis exchange of carboxylato ligands are manifold and again analogous to nanoparticle chemistry. Four potential cases are as follows:

1. Similar to what has been discussed before for nanoparticles, certain ligands cannot be introduced directly during the cluster synthesis. An example is the superparamagnetic cluster $Mn_{12}O_{12}(OAc)_{16}$ which is prepared by oxidation of $Mn(OAc)_2$. Carboxylato ligands from less readily available or oxidation-sensitive Mn(II) carboxylates can be introduced by post-synthesis ligand exchange [26].
2. Related to the previous case is the preparation of metal–organic framework (MOF) structures with clusters as connector units. One preparative approach uses clusters with monofunctional ligands as starting compounds followed by exchange of the ligands against di- or tricarboxylate units to connect the cluster units with each other and form the network structures. Illustrative examples are the reaction of $[Fe_3O(OAc)_6L_3]^+$ (L = neutral ligands) with various dicarboxylic acids HOOC-R-COOH [27,28] (Fig. 5) or the reaction of $Zr_6O_4(OH)_4(OMc)_{12}$ with muconic or terephthalic acid [29]. Acetic or methacrylic acid is liberated and porous MOF networks are formed. The cluster units are intact after carboxylate exchange in both cases.
3. Deliberate *partial* exchange of ligands can be used to control the ratio of reactive and non-reactive ligands when the clusters are used for the preparation of cluster-reinforced organic polymers [30,31]. It was shown, for example, that some properties of the polymers obtained by photopolymerization of $Zr_4O_2(OMc)_{12-x}(pivalate)_x$ and 2-hydroxyethyl methacrylate, such as induction period of photopolymerization, storage and loss modulus, swellability or glass transition temperature, depend on the number of polymerizable OMc ligands per cluster, i.e., the crosslinking ability of the cluster. [32].
4. Partial exchange of functional carboxylato ligands by carboxylates with a different organic functionality results in clusters with dual functionalities. Copolymers with 2- and 3-dimensional structures in the nm range were produced by

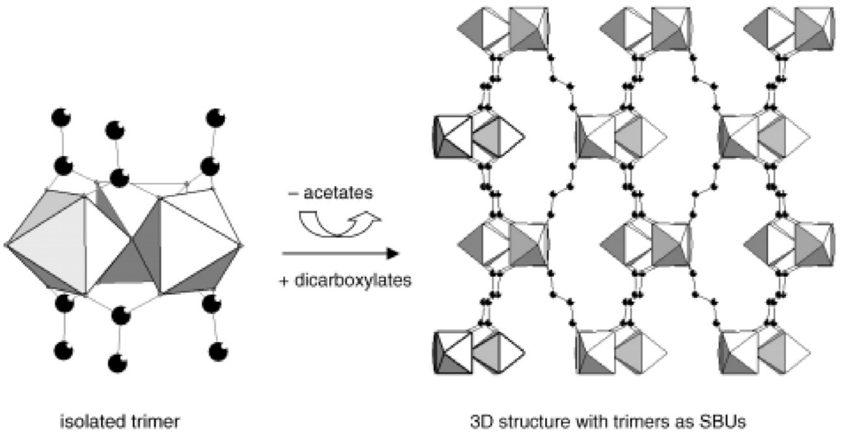

Fig. 5. MOF formation by reaction of $[Fe_3O(OAc)_6L_3]^+$ with dicarboxylic acids [27].

STED-lithography from pentaerythritol triacrylate and the clusters $Zr_4O_2(OMc)_{12-x}(OOC\text{-}CH_2CH_2SH)_x$. The mixed-ligand cluster was obtained by partially exchanging OMc ligands against 3-mercaptopropionato ligands. The OMc ligands participate in the polymerization reaction, while the mercapto groups serve as anchor points for further functionalization after polymer formation [33].

Given the fact that retention of the cluster core composition and structure during a particular ligand exchange experiment is not always self-evident, integrity of the cluster core has to be checked in every case. This is not trivial in many cases, due to the lack of suitable and easy to apply spectroscopic methods. The clusters can be unequivocally identified by EXAFS [34], but this method cannot be applied routinely. ^1H and ^{13}C NMR spectroscopy only gives relevant information if the ligands are not dynamic and an informative set of ligand signals is obtained (as discussed above for the low-temperature spectrum of $Zr_4O_2(OMc)_{12}$). In the infrared spectra, characteristic bands of the cluster core (in the MIR and FIR region) are difficult to identify, and bands of the ligands provide no relevant information. In order to identify the bands of the cluster core, DFT calculations on $Zr_4O_2(OMc)_{12}$ were performed with the crystallographically determined structure as input [35]. The thus identified bands of the cluster core were then used to confirm that the cluster core was retained after ligand exchange with pivalic acid, by which the cluster $Zr_4O_2(OPiv)_{12}$ (OPiv = pivalate) was obtained.

Exchange reactions of coordinatively bonded ligands (L, L′) are equilibria (Eq. (1) with anionic ligands L and L′) as for monometallic complexes and therefore the composition of the reaction mixture can be shifted to one side or the other by changing the concentrations of H-L or H-L′. The required excess of H-L or H-L′ for completely shifting the equilibrium to one side or the other depends on the magnitude of the equilibrium constant. If the cluster core (M_xO_y) was retained during the exchange reaction (left to right in Eq. (1)), then re-exchange of the ligands L′ of isolated $M_xO_yL_{z-n}L'_n$ (right to left in Eq. (1)) should result in the original cluster $M_xO_yL_z$, thus proving that the cluster core is retained during ligand exchange.

$$M_xO_yL_z + n\ H\text{-}L' \rightleftarrows M_xO_yL_{z\text{-}n}L'_n + n\ H\text{-}L \qquad (1)$$

Such exchange/re-exchange experiments were performed for the cluster pairs $Ti_8O_8(OOCPh)_8/Ti_8O_8(OAc)_8$ [36] and $Zr_4O_2(OMc)_{12}/Zr_4O_2(OPiv)_{12}$ [35]. The starting clusters were reacted with an excess of the other acid, the cluster with completely exchanged carboxylato ligands were isolated and then treated with an excess of the former acid, by which the starting cluster was restored. NMR spectra and X-ray structure analyses proved that the cluster pairs had the same structure. The exchange experiments can be stopped at intermediate stages to give the mixed-ligand clusters $Ti_8O_8(OOCPh)_{8-x}(OAc)_x$ or $Zr_4O_2(OMc)_{12-x}(OPiv)_x$ which accordingly have the same structure as the parent clusters.

3.2. Mechanism of carboxylate exchange

A possible mechanism for the carboxylate exchange can be derived from the structures of the two derivatives $Zr_6O_4(OH)_4(OOCR)_{12}(HOX)$ (X = H, Bu) [37]. Their structures are very similar to that of $Zr_6O_4(OH)_4(OMc)_{12}$, but one bridging OOCR is converted into a monodentate ligand. The coordination site thus vacated at the neighboring Zr atom is occupied by the H_2O or BuOH molecule, which forms a hydrogen bridge to the monodentate OOCR ligand (Fig. 6).

Taking this ligand arrangement into account, one can imagine the following sequence of events for exchange reactions between carboxylato-substituted oxo clusters and carboxylic acids: (i) change of the coordination of the original carboxylato ligand (OOCR) from η_2 to η_1 and (ii) concomitant addition of H-OOCR′ to the vacated coordination site similar to the coordination of HOX in Fig. 6, (iii) proton transfer between entering (OOCR′) and leaving (OOCR) carboxylate group, (iv) elimination of H-OOCR and (v) change of the coordination of OOCR′ from η_1 to η_2 (Fig. 7). A similar mechanism can be imagined for chelating ligands.

There are of course several other mechanistic possibilities for the carboxylate exchange. For example, when solutions of equimolar amounts of $Zr_4O_2(OMc)_{12}$ and $Zr_4O_2(OPiv)_{12}$ were mixed, the mixed-ligand cluster $Zr_4O_2(OMc)_6(OPiv)_6$ was formed [35]. The mechanism of this scrambling reaction must be different to the one in Fig. 7 because no protic compounds are involved. A plausible mechanism would be the intermediate formation of carboxylato bridges between the two cluster cores.

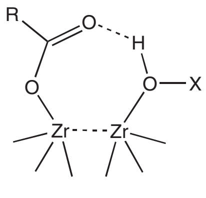

Fig. 6. Bonding of the $[ROO\cdots H\text{-}OX]^-$ entity in the clusters $Zr_6O_4(OH)_4(OOCR)_{12}(HOX)$.

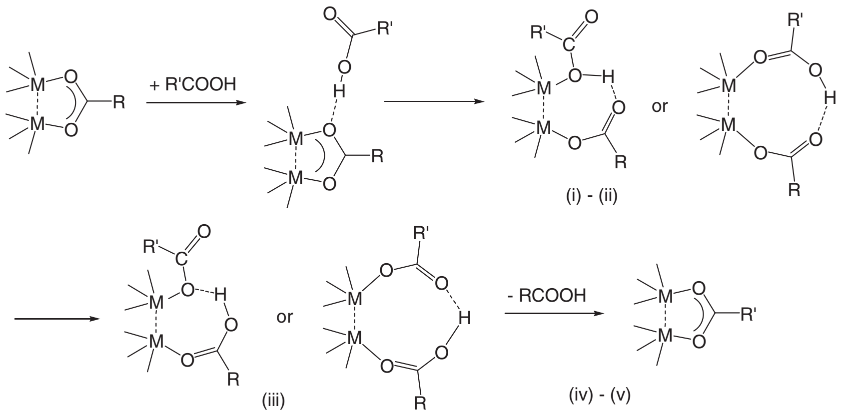

Fig. 7. Possible mechanism for carboxylate exchange reactions.

4. Ligand influence on the cluster properties

Organic groups bonded to the surface atoms may influence physical (optoelectronic, magnetic, etc.) properties of nanoparticles to a considerable extent. Varying the nature of the surface ligands changes the electronic properties of the surface atoms and, due to the high proportion of surface atoms, also the electronic structure of the whole particle. A recent example is the energy level modification of 3.5 nm PbS nanoparticles upon changing the surface ligands, where shifts by up to 0.9 eV were observed [38].

For the same reasons, similar effects must be expected for clusters, albeit only few systematic investigations exist. The cluster core of $Ti_6O_4(OiPr)_{10}(OOCR')_2(O_3PR)_2$ is very robust and many derivatives with various phosphonato [8] and carboxylato ligands [39] were prepared and structurally characterized. As mentioned above, no ligand dynamics was observed at room temperature. In a series of 13 derivatives of $Ti_6O_4(OiPr)_{10}(OOCR')_2(O_3PPh)_2$ with different carboxylato ligands, gradual reduction of the cluster bandgap by up to 0.5 eV with an increasing electron-withdrawing effect of the carboxylato ligands was observed [39].

One of the best investigated types of carboxylato-substituted metal oxo clusters is the $Mn_{12}O_{12}(OOCR)_{16}$ family with interesting magnetic properties (single molecule magnets). The redox potentials of a series of $Mn_{12}O_{12}(OOC\text{-}C_6H_4R')_{16}$ clusters with different aryl substituents R′ depended on the kind of carboxylato ligand. Furthermore, while all derivatives exhibited both the first oxidation and the first reduction waves in cyclic voltammograms and differential pulse voltammograms, the second oxidation and the second and third reduction waves was only present for particular ligands [40]. A ligand influence on the magnetic properties of such clusters is difficult to investigate because of different numbers of co-crystallizing disordered solvent molecules [26, 41].

5. Surface functionalities

Another important function of the surface groups of nanostructures is to furnish (mostly organic) functionalities with complementary properties. A good example is again the aforementioned sensitizer-decorated titania nanoparticles [15], where only the tuned interplay between the nanostructures and the sensitizing units results in the photovoltaic performance.

The same is again true for clusters. In the case of carboxylato-substituted metal oxo clusters, the option of cluster functionalization was mainly exercised for clusters with polymerizable carboxylato ligands as precursors for cluster-reinforced polymers. The kind of functional group depends on the polymerization method, such as radical polymerization, atom-transfer radical polymerization, ring-opening metathesis polymerization, thiol-ene reactions, etc. Clusters with polymerizable carboxylato ligands and the resulting polymers were extensively reviewed elsewhere [30,31]; a repetition of this discussion would exceed the scope of the current article.

Apart from polymerizable ligands little attention was up to now paid to the possibilities offered by other functional groups. An example are the clusters $Zr_4O_2(OMc)_{12-x}(OOC\text{-}CH_2CH_2SH)_x$ mentioned before, where the terminal SH groups were used to anchor fluorescence markers [33].

Quite a few metal oxo clusters have OR or (less often) OH coligands, which can also be taken as reactive sites on the cluster surface. Although it is known that most OR-substituted clusters are moisture-sensitive (unless they are embedded in a polymeric matrix), no controlled hydrolysis reactions were carried out so far, and therefore it is not known whether this might lead to new clusters or cluster assemblies. Investigation of $Ti_6O_4(OEt)_8(OMc)_8$ by electrospray TOF mass spectrometry showed that ether elimination with concomitant formation of new oxo groups and smaller clusters is one of the decomposition pathways [42].

The most prominent cluster types with OH groups are $Zr_6(OH)_4O_4(OOCR)_{12}$ and $[Zr_6(OH)_4O_4(OOCR)_{12}]_2$ (which cannot be converted into each other [43]). Nearly all known clusters of this type co-crystallize with hydrogen-bonded carboxylic acid molecules (see Section 2). The fact that the μ_3-OH groups are fairly acidic, acting as hydrogen donors to the CO groups of the carboxylic acid molecules, has been utilized to attach other metals to the Zr_6O_8 cluster core. Reaction of Fe(III), Mn(III), Ni(II) and Co (II) carboxylate or nitrate [44,45] with $Zr_6(OH)_4O_4(OOCR)_{12}$ in the presence of auxiliary ligands resulted in deprotonation of some or all μ_3-OH groups and coordination of two, three or six metal cations to the μ_3-O sites (*i.e.*, conversion of the -OH into -OM units) (Fig. 8).

A cluster with a related structure, *viz.* $Zr_{10}O_8(OBu)_{16}(OOC\text{-}C_6H_4CH_2Cl)_8$, was obtained by reaction of $Zr(OBu)_4$ and 4-(chloromethyl)benzoic acid [46]. In a formal sense, this cluster is formed by condensation of $Zr(OBu)_4$ units to the μ_3-OH groups of $Zr_6O_4(OH)_4$ core with partial replacement of four carboxylato ligands (for reasons of charge neutrality). The —OH groups are thus converted into —OZr units. Although this cluster was formed *in situ*, rather than reaction of isolated $Zr_6O_4(OH)_4(OOCR)_{12}$ with metal salts as in the previous example, formation of the Zr_{10} cluster my proceed similarly.

Indirect evidence for the formation of larger cluster units by condensation reactions involving cluster M-OH groups was also

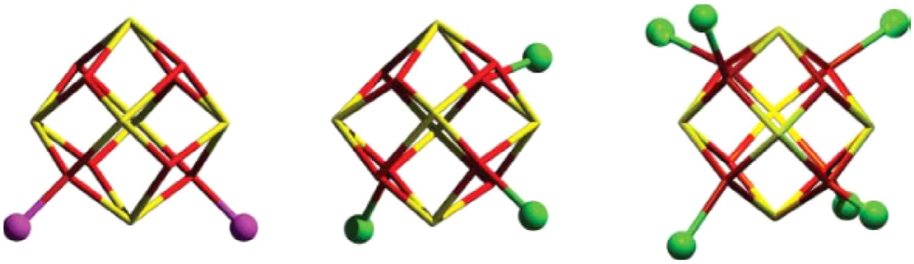

Fig. 8. The $M_nZr_6O_8$ core structures with two M(III) (left), three Ni(II) (center) and six Ni(II) heteroatoms (Zr: yellow, O: red, M: purple, Ni: green) [44]. The organic ligands were omitted for clarity.

obtained when $[Zr_6O_4(OH)_4(OOCEt)_{12}]_2$ was reacted with N-methyldiethanolamine, 4,4′-bipyridine and Co or Ni nitrate. It was postulated that in a first step the $[Zr_6]_2$ cluster (see Fig. 4 for a related structure) undergoes intramolecular condensation resulting in $[Zr_{12}O_{11}(OH)_{11}(OOCEt)_{16}]^-$ units followed by coordination of three M(II) units and subsequent connection of two such $Zr_{12}M_3$ units through two 4,4′-bipyridine ligands [47].

6. Concluding remarks

Clusters are the link between classical coordination compounds and nanosystems, as they combine features of both. A better understanding of the surface chemistry of nanostructures is more and more recognized as one of the key requirements for developing purpose-built nanosystems with structures and properties as reproducible as those of molecules. However, we are currently far away from having enough and comprehensive information. It was shown in this article, that there are many analogies between the surface chemistry of clusters and nanoparticles having the same chemical composition. Although the surface chemistry of clusters is also still in its infancy, there is a chance of gaining a sufficient amount of knowledge much faster, because clusters are easier prepared and investigated.

Acknowledgements

The author's own work has been supported by several grants from the Austrian Science Funds (FWF).

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