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# Synthesis and Structural Determination of a Hexanuclear Zirconium Glycine Compound Formed in Aqueous Solution

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Single crystals of a zirconium−glycine compound have been first grown in aqueous solution via an excess acid and extra stabilizer approach. The crystal structure $[Zr_6(OH^-)_8(H_2O)_8(HGly)_4(Gly^-)_4]\cdot(SO_4^{2-})_6\cdot 14H_2O$ (**CP-1**) has been characterized by single-crystal X-ray diffraction. The structure revealed that it is composed of hexa-zirconium octahedral clusters coordinated by eight carboxylic acid groups of glycine. The charge assignment is also consistent with the electronic structure calculations, and the computational result reveals that the $Zr_6$ core should have no skeleton electrons.

The zirconium−aluminum−glycine (ZAG) complex is an efficacious antiperspirant salt that has been sold in the marketplace for nearly half a century.[1] To date, no structural information of zirconium with glycine as a gelation inhibitor or stabilizing "buffer" has been reported. Consequently, the lack of structural knowledge has significantly hindered researchers' efforts to improve the efficacy of the ZAG salt. Furthermore, knowing the structure of zirconium−amino acid complexes should help chemists and biologists understand the nature of metal−ligand interactions in aqueous solutions and further ascertain Zr binding sites in folded proteins.[2] It should also help scientists understand such important processes as the hydrolysis of peptides/proteins[3] and the immobilization of enzymes.[4]

By virtue of the strong acidity of the zirconium cation resulting from its large charge/size ratio, this metal possesses a remarkable tendency to hydrolyze even in a pH range of 0−3.[5] To prevent its hydrolysis, anhydrous organic solvents and anaerobic conditions are typically employed in their synthesis. The organic solvents act as reaction media, an environment for which a number of remarkable Zr cationic clusters of tetra, hexa, octa, and even larger clusters have been synthesized.[6] Nevertheless, there are aqueous-based methods that have been reported to produce Zr clusters. The first applies basic solutions to allow zirconium to form anionic oxoclusters.[7] The second purposely selects multichelating ligands to generate mononuclear Zr species.[8] Not surprisingly, the inherent hydrolysis tendency of the zirconium cations blocks an effective route to explore unknown zirconium structures in aqueous solution. The challenge served as a motivation for us to find a new approach to the synthesis of zirconium compounds, especially with amino acids in aqueous solutions.

Recent studies have revealed that, as the solution concentration increases, zirconium hydrolysis causes the metal ions

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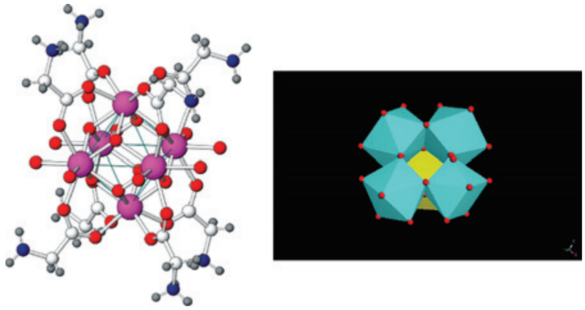

**Figure 1.** (a) A cation of structure of **CP-1**. The counterions and solvent molecules are omitted for clarity. The color code is zirconium (purple), oxygen (red), nitrogen (blue), carbon (light gray), hydrogen (gray). (b) View of connections of four Zr-centered polyhedra in the equatorial plane (blue) and one apical Zr-centered polyhedron (yellow). The top Zr polyhedron is omitted for showing edge-sharing geometry.

to form multinuclear rather than mononuclear species.[9–11] These multinuclear clusters are predominant even at low pH levels in aqueous solutions. For example, the tetrameric $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ species has been confirmed to be the dominate species in low-pH solutions.[9] Small-angle X-ray scattering measurements revealed that the octameric $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ species was predominant and in equilibrium with the tetramer species when the pH was raised to 0.6.[10] With increasing hydrolysis, a 2D sheetlike structure forms[11] before hydrolyzing further to give rise to a polymeric gel or precipitate.

The present accepted structure of Zr compounds with amino acids is thought to be derived from the above tetrameric Zr−$H_2O$ cluster in which amino acids simply replace the 16 terminal water ligands to give rise to a $Zr_4(Gly)_8$ cluster in a 1:2 ratio. The proposed structure is based on limited spectroscopic results.[12]

In this contribution, we report the preparation and structure of a Zr−glycine compound which is a new hexa cationic cluster obtained via an excess acid and extra stabilizer (EAES) strategy. Hydrated zirconium oxide chloride, glycine, and sulfuric acid in a molar ratio of 1:14.07:2.76 were mixed in an aqueous solution at pH 2.52. Insoluble colorless column-like crystals were formed after several days. The crystals turned opaque and decayed due to the loss of solvent after being taken out of the mother liquor for a few minutes (Supporting Information). For this reason, a high-quality crystal was sealed in a glass capillary together with the mother liquor for data collection. The IR spectrum showed two peaks at 1587 and 1460 cm$^{-1}$, which were assigned to $\nu_{as}$ COO$^-$ and $\nu_a$ COO$^-$, respectively. The structure of the title compound (Figure 1), with the formula $[Zr_6(OH^-)_8(H_2O)_8(HGly)_4(Gly)_4]\cdot(SO_4^{2-})_6\cdot 14H_2O$, hereafter labeled as **CP-1** (CP standing for Colgate-Palmolive), was determined by single-crystal X-ray diffraction.[13] This structure consists of a hexanuclear zirconium core $[Zr_6(OH)_8]^{12+}$ with a pseudo $D_{4h}$ symmetry. The cluster is a slightly flattened octahedron. See Table 1 for crystallographic data.

**Table 1.** Selected Crystallographic Data for **CP-1**

| | |
|---|---|
| empirical formula | $C_{16}H_{88}N_8O_{70}S_6Zr_6$ |
| fw | 2252.62 |
| $T$/K | 203(2) |
| space group | $C2/m$ |
| $a$ (Å) | 24.979(4) |
| $b$ (Å) | 11.4356(17) |
| $c$ (Å) | 13.725(2) |
| α (deg) | 90 |
| $\beta$ (deg) | 115.902(2) |
| $\gamma$ (deg) | 90° |
| $Z$ | 2 |
| $D_{calc}$ (g cm$^{-1}$) | 2.121 |
| $\mu$ (mm$^{-1}$) | 1.173 |
| R1 | 0.0699 |
| wR2 | 0.1706 |

The zirconium atoms form the corners of the octahedron. The eight faces of the octahedron are capped by the $\mu_3$-OH$^-$ groups. In addition to these groups, there are eight ligands attached to each octahedron corner. These eight ligands at the apical corners are the oxygen atoms from the carboxylic groups of Gly, while at the equatorial corners, only two are from the carboxylic groups. The remaining two are from $H_2O$, with the Zr−O distances of 2.203−2.211 Å. The eight vertical edges of the flattened octahedron are bridged by the glycine ligands, whereas the four equatorial edges are not bridged. This cluster, illustrated in Figure 1, is very different from the previously proposed tetrameric cluster.[12] In the $Zr_6$ cluster, the Zr−Zr distances of 3.524−3.528 Å at the apical edges are slightly shorter than those of the Zr−Zr contacts of 3.549−3.554 Å in the equatorial plane. The eight $\mu_3$-OH$^-$ groups have similar coordination geometries compared to that of other $\mu_3$-OH$^-$ species reported in the literature.[6f] The typical bond distances of Zr(IV)−OH$^-$ in the range of 2.146−2.194 Å are shorter than the those of Zr(IV) with the oxygen atoms of the bridging carboxylic groups (2.222−2.269 Å). The average bond angles of the $\mu_3$-OH$^-$ coordination (109.16°) are close to the tetrahedral angle of 109°, but smaller than that of $\mu_3$-O (>113°).[6h] The four equatorial Zr(IV) corners are connected to the apical Zr(IV) ones by eight carboxylic groups of different glycine molecules in a *syn−syn* mode. The four Zr-centered polyhedra in the equatorial plane are connected to each other by sharing one edge and are connected to the apical Zr by sharing four

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(13) (a) Diffraction data were collected on a Bruker SMART CCD diffractometer with Mo K$_\alpha$ radiation ($\lambda$ = 0.710 73 Å) at 203(2) K. The structure was solved by direct methods with the SIR97 program[13b] and refined by full-matrix least-squares treatment again $F^2$ using the SHELXTL program suite.[13c] Absorption corrections were applied empirically using the SADABS program.[13d] CCDC-659843 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A non-disordered model is also supplied in the Supporting Information. The R1 and wR2 values for the non-disordered model are 0.086 and 0.214, respectively. (b) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115. (c) Sheldrick, G. M. *SHELXTL*, version 6.10; Bruker Analytical Instruments Inc.: Madison, WI, 2000. (d) Sheldrick, G. M. *SADABS*, version 2.03; University of Göttingen: Göttingen, Germany, 2007.

edges. As is well-known, glycine can exist as either a neutral HGly: ($^{-}$OOC$-$CH$_2$$-$NH$_3^+$) or an anion form Gly: ($^{-}$OOC$-$CH$_2$$-$NH$_2$). Both neutral and anion modes of the amino acid can coexist in one structure to meet overall charge balance requirements.[14] Two glycine molecules on the left side at the upper half of the Zr$_6$ octahedron are assigned as neutral, while two on the other side are assigned as anionic. At the lower half of the octahedron, the assignment is reversed (Figure 1a). These assignments are based on the C$-$C and C$-$N distances reported for neutral and anionic glycine. The C$-$C distance is slightly shorter and the C$-$N distance slightly longer in the anionic form of glycine.[15] Examination of the structure revealed that the C$-$C and C$-$N bond lengths of four glycines are 1.520 and 1.479 Å, corresponding to $^{-}$OOC$-$CH$_2$$-$NH$_3^+$, while those of the remaining four glycines are 1.520 and 1.470 Å, corresponding to $^{-}$OOC$-$CH$_2$$-$NH$_2$. The size of the hexanuclear cluster is *ca*. 13.4 Å. There are six sulfate ions corresponding to each Zr$_6$ cluster in the unit cell as counterions for charge balance and 14 water molecules engaged in a number of hydrogen bonds in the structure.

The charge assignment is also consistent with our electronic structure calculations. It is well-known that, in an M$_6$X$_8$ (M$_6$ octahedron with all faces capped by X ligands) or M$_6$X$_{12}$ (M$_6$ octahedron with all edges bridged by X ligands) type cluster, there exist 11 (for M$_6$X$_8$) or 8 (for M$_6$X$_{12}$) M$-$M bonding and M$-$X nonbonding molecular orbitals.[16] These orbitals can accommodate additional skeleton electrons. In the case of our compound, only one low-lying orbital of $a_{1g}$ symmetry is of M$-$M bonding. The others are high in energy due to additional terminal ligands (four on each Zr). This orbital, however, is of Zr$-$O antibonding character where the oxygen is the octahedron face-capping ligand. The molecular orbital overlap population (MOOP)[17a] diagram calculated by the extended Hückel method[17] is shown in Figure 2. In this figure, the calculated MOOPs for the Zr$-$Zr and Zr$-$O (face-capping) bonds in the experimentally determined structure are plotted on the left and right half of the graph, respectively. The lowest unoccupied molecular orbital of pseudo $a_{1g}$ symmetry in the cluster of the $D_{4h}$ point group is indeed of Zr$-$Zr bonding and Zr$-$O (face-capping) antibonding character. The computational result reveals that the Zr$_6$ core should have no skeleton electrons.

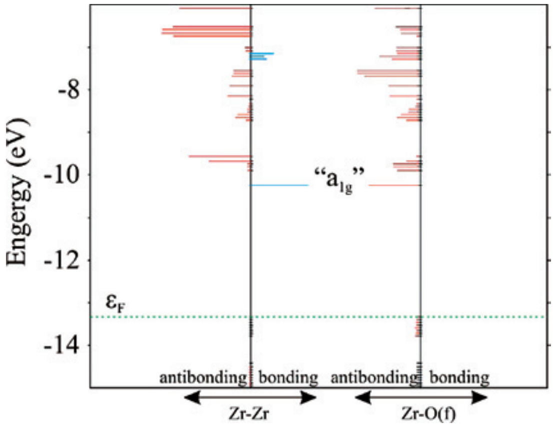

**Figure 2.** MOOPs of the Zr$-$Zr and Zr$-$O (face capping) bonds calculated for the experimentally determined structure.

In summary, we have successfully synthesized and characterized the first Zr$-$glycine-based crystal structure with a Zr-to-glycine ratio of 3:4 that is quite different from the previously proposed tetranuclear cluster structures. The structural information will provide us a better understanding of the interactions of Zr with amino acids in cluster compounds. The present methodology (EAES) provides a practical synthetic route and can be extended to the preparation of more hydrated Zr complexes in aqueous solutions.

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**Supporting Information Available:** Additional figures, tables, and methods and X-ray crystallographic file for CP-1 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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