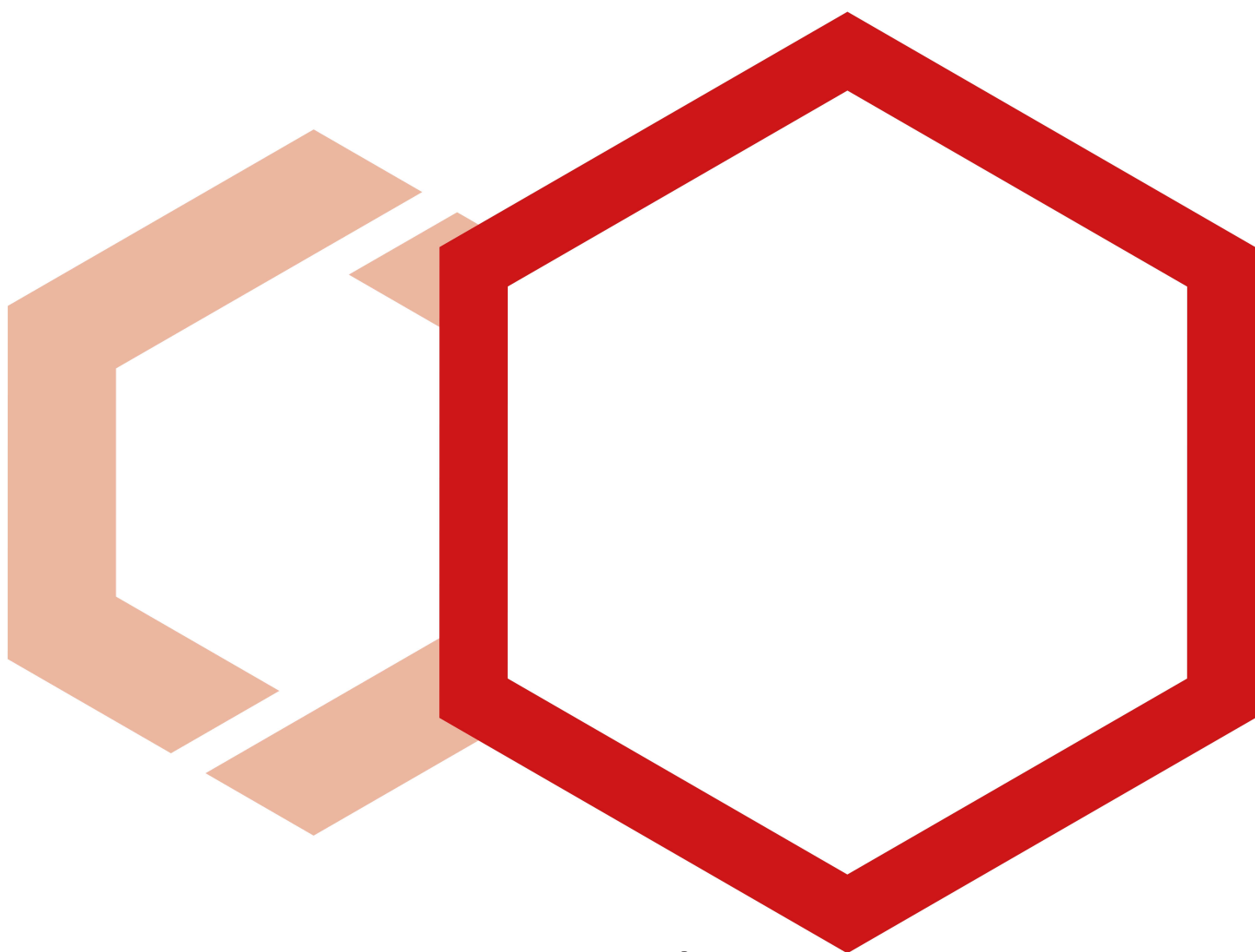




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Structural Characterization of a High-Nuclearity Niobium(V) Carboxylate Cluster Based on Pivalic Acid

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We report a novel Nb(V)–carboxylate cluster obtained from reaction of niobium(V) ethoxide and pivalic (trimethylacetic) acid. Single crystal X-ray diffraction data reveal a structure composed of 16 Nb(V) ions featuring oxo-, ethoxy- and pivalate moieties. The new cluster exhibits the highest nuclearity among structurally characterized niobium carboxylates reported to date.

Keywords: carboxylate ligands, cluster compounds, niobium, pivalate, structure elucidation.

Introduction

Metal carboxylates are one of the most widely studied classes of compounds, their history going back to the early days of modern inorganic chemistry.^[1] Owing its ability to act either as a mono- or bidentate, each further exhibiting both chelating and bridging modes,^[2] the RCOO[−] moiety offers a rich structural chemistry. The bridging character was extensively utilized in fundamental studies of magnetic exchange interactions^[3] and metal-metal multiple bonding,^[4] properties which require tailored proximal metal sites. Furthermore, the ability of the carboxylate ligand to support multinuclear clusters enables formation of high-spin transition metal clusters exhibiting single molecule magnet behavior.^[5]

The emergence of metal-organic frameworks (MOFs)^[6–12] provided another reason for continuing interest in the preparation of metal carboxylate clusters and their characterization. With typical MOFs assembled from inorganic metal nodes (also known as secondary building units or SBUs) bound together by multitopic carboxylic acids (linkers), these molecular clusters can provide insight into MOF structure and reactivity, as well as influence the dynamics of

respective framework formation. A breakthrough in the preparation of the early-transition metal-based carboxylate frameworks exemplifies the latter: the addition of a modulating agent, commonly a mono-carboxylic acid, in the reaction mixture is necessary to obtain highly crystalline MOFs instead of amorphous powders.^[13–16] This ‘modulated synthesis’ conceivably proceeds through intermediate formation of the soluble modulator-terminated carboxylates (or even SBU analogues), which then slowly exchange the capping ligands for the multitopic carboxylate, leading to the final crystalline product. Consistent with this mechanism, some early-transition metal MOFs can be made directly from discrete isolated metal carboxylate clusters.^[17,18]

Niobium has a highly oxophilic character (particularly in higher oxidation states), large covalent radius, and fluxional coordination sphere,^[19] rendering the controlled precipitation of well-defined crystalline solids in classical *de novo* fashion challenging.^[20,21] Tellingly, only few instances of niobium incorporation into MOFs have been reported so far^[22–26] with only one recent example of mono-metallic *de novo* synthesized framework, which is based on deprotonated 3,6-dichloro-2,5-dihydroxybenzoquinone rather than a carboxylate linker.^[27] Partly driven by the surprising lack of carboxylate-based Nb MOFs, we sought to explore the fundamental carboxylate chemistry of niobium, including Nb clusters. Here, we document the discovery of a

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niobium pivalate (piv) cluster derived from niobium (V) ethoxide, which displays the highest nuclearity among carboxylate-supported Nb systems.

Results and Discussion

Heating niobium(V) ethoxide with pivalic acid in anhydrous acetonitrile for several days followed by slow cooling of the reaction mixture resulted in the precipitation of colorless plates. Single crystal X-ray

diffraction analysis revealed a novel niobium carboxylate cluster, $\text{Nb}_{16}(\text{O})_{28}(\text{OEt})_{12}(\text{piv})_{12}$ (Figures 1,c and 1,d). The structure can be viewed as a combination of a core unit (CU, Figure 1,a) and four distorted square pyramidal peripheral units (PUs, Figure 1,b), where two of the Nb vertices are shared with the core. The core unit (Figure 2,a) is assembled from four Nb(V) centers (Nb(3) and Nb(4) along with their symmetry related pairs) and four bridging oxo species (three of them being unique). Despite the anhydrous conditions, the formation of oxo linkages is possible through scrambling of two alkoxide-containing molecules^[28] and/or the esterification pathway involving *in situ* formation of ethyl pivalate and water, which can subsequently react with the niobium-containing species.^[29] The conformation of this unit can be described as a boat-boat arrangement,^[30] featuring similar Nb–O bond lengths (estimated standard deviations for all of the interatomic distances are listed in Table S2) with an average of 1.918 Å. This value is in good agreement with previously reported niobium carboxylates featuring tetranuclear Nb(V) arrangements with μ_2 -oxo linkages.^[29,31] The nearly ideal octahedral coordination sphere of these niobium(V) centers is saturated with μ_2 -oxo ligands connecting to two PUs.

Although these PUs (for representative structure see Figure 2,b) have the same connectivity, one resides fully in the asymmetric unit, while two of them lie on a mirror plane bisecting the cluster. We will limit the discussion in the text to the former; the relevant distances for the remaining PUs are comparable with similar trends and are listed in Table S2. The representative PU adds three Nb(V) centers ligated with oxo, ethoxy and pivalate moieties. Interestingly, the three Nb(V) centers are connected through a μ_3 -oxo ligand, which to date has only been reported in carboxylate supported systems for Cotton's bi-oxo-capped triangular cluster derived from a Nb(III) precursor^[32] and for an embonate-decorated species published recently.^[33] The degree of displacement of bridging O(11) from the plane outlined by Nb(V) centers falls in-between the literature values, at 0.236 Å. The distances between the metal centers and O(11) are slightly asymmetric with Nb(7) and Nb(8) being similar and averaging 2.075 Å while the Nb(9)–O(11) bond length measures 2.039 Å. These metrics are in line with the aforementioned literature examples.

The structural differences between the Nb(7), Nb(8) pair and Nb(9) arise from connectivity with the core unit and among the metal centers themselves. Nb(9) is bound to both Nb(3) and Nb(4) through μ_2 -oxo ligands (O(9) and O(10)), whereas Nb(7) and Nb(8) are bound

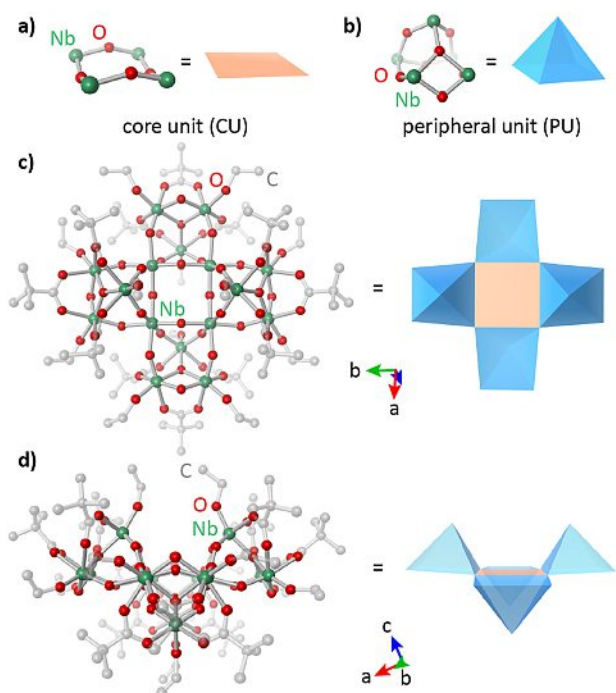


Figure 1. Overview of $\text{Nb}_{16}(\text{O})_{28}(\text{OEt})_{12}(\text{piv})_{12}$ structure. Hydrogen atoms and solvent molecules were omitted for clarity.

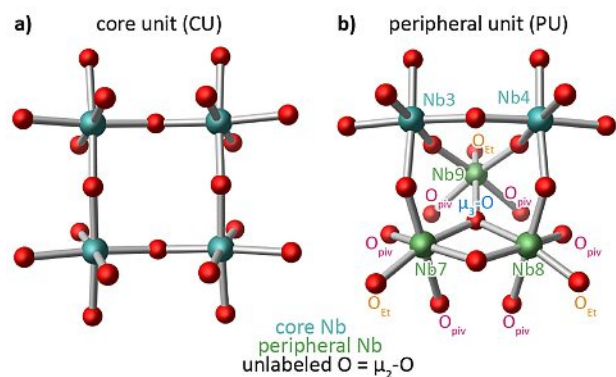


Figure 2. Detailed view of the units present in the cluster.

to Nb(3) (through O(7)) and Nb(4) (through O(8)), respectively. The lower connectivity for this pair of Nb(V) centers is compensated by the presence of a μ_2 -oxo bridge between them (O(12)). It is worth highlighting that the Nb–O distances constituting Nb(9)–O(9)–Nb(3) (Nb(9)–O(10)–Nb(4)) linkages are more symmetric than for Nb(7)–O(7)–Nb(3) (Nb(8)–O(8)–Nb(4)). The PU is terminated with three piv moieties and three ethoxides. One ethoxide caps each Nb center, while carboxylates bridge pairs of metal centers. All Nb–O_{Et} distances are similar and average 1.858 Å. Whereas the oxygen atoms of the bidentate pivalate bridging Nb(7) and Nb(8) are essentially equidistant (2.198 Å averaged) from the closest metal center, the analogous bonds for the pivalates connecting Nb(9) to the Nb(7) and Nb(8) differ slightly in length (2.091 vs. 2.180 Å) and result in tilting of the carboxylate ligand.

The most notable feature of the described complex is its nuclearity, which is highest to date for structurally characterized niobium carboxylates. Niobium has been shown to form remarkably high-nuclearity polyoxoanions (known as polyoxoniobates) such as the recently reported species containing 114^[34] and 288^[35] niobium centers. In contrast to the purely inorganic polyoxoniobates, carboxylate-terminate clusters display much smaller nuclearity; prior to this report the largest nuclearity was a dodecanuclear carboxylate cluster.^[33]

Conclusions

In this contribution, we described the structure of a new Nb(V) carboxylate cluster containing the highest number of niobium centers to date. With its 16 metal centers, the complex reported herein sets the new bar for high-nuclearity carboxylate-supported niobium systems and expands our grasp of the coordination chemistry of this element, which continues to surprise. The mere existence of this complex hints its potential importance in solution-based syntheses of extended carboxylate-based materials such as MOFs, particularly in combination with a modulator approach.

Supplementary Material

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/hlca.202000186>. CCDC-2026550 contains the supplementary crystallographic data for this work. These data can be obtained free of charge from *The Cambridge*

Crystallographic Data Centre through <https://www.ccdc.cam.ac.uk/structures/>

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Author Contribution Statement

M. D. K. and *M. D.* conceptualized the project. *M. D. K.* performed the synthetic work. *L. S. X.* solved and refined the crystal structure. All authors were involved in writing of the manuscript and approved its final version.

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