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Synthesis and Crystallization of Infinite Indium and Gallium Acetate 1D Chain Structures and Concomitant Ethyl Acetate Hydrolysis

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Two unusual complexes of formula $[M(\mu\text{-OH})(\mu\text{-}O_2CCH_3)_2]_n$ [M = In (**1**) or Ga (**2**)] were crystallized by diffusion of ethyl acetate into methanolic solutions of the $M(NO_3)_3$ salts and *N*-nitrosopyrrolidine. They represent the first examples of such simple group 13 containing structures comprising 1D chains, and their formation results from the surprising hydrolysis of ethyl acetate to provide the bridging acetate ligands.

Interest in the area of infinite group 13 carboxylate compounds originates from several areas, stimulated largely by work on metal−organic frameworks and zeolites.[1−5] Numerous examples of 1D, 2D, and 3D indium (and fewer of gallium) carboxylate extended structures exist, often taking advantage of benzene di- and tricarboxylates.[6−15] In these cases, the ligand geometry seems to have a dominant effect on the final extended structure.[13] The steric bulk of the bridging ligands also plays a role, with *tert*-butyl or otherwise substituted ligands often forming rings instead of chains.[16,17] One structure type was notably absent from this literature—a truly 1D chain of gallium or indium with bridging acetate and hydroxide—a surprising omission given the interest in chain structures comprising group 13 elements.[18−20]

In addition to the multidimensional extended indium structures mentioned above, there are examples of nonlinear discrete structures of group 13 ions, such as an elegant "gallic wheel" produced by Christou and co-workers.[17] The metal ions in these "gallic wheel" and indium carboxylate structures possess coordination environments similar to those of the 1D chain structures presented in this Communication but form more complicated extended structures.[6,12] Several additional reports have detailed a related manganese 1D chain structure, which is the only other example of this infinite linear-chain topology with acetate and hydroxide that we have encountered.[21−24] A recent report describes a structure similar to that of the indium chain but with iodate bridging ligands in place of acetate.[25]

Herein, we report two new infinite chain structures of formulas $[In(\mu\text{-OH})(\mu\text{-}O_2CCH_3)_2]_n$ (**1**; Figure 1) and $\{[Ga(\mu\text{-OH})(\mu\text{-}O_2CCH_3)_2]\cdot HOAc\cdot H_2O\}_n$ (**2**). To the best of our knowledge, **1** and **2** are the first examples of such acetate-hydroxy-bridged chain compounds comprising group 13 metals and also showcase an interesting reaction wherein

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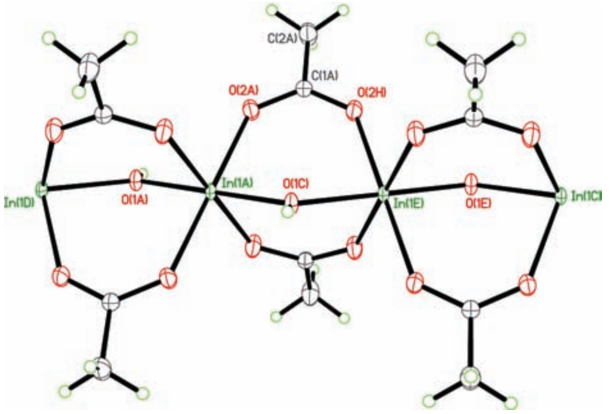

Figure 1. ORTEP diagram (50% probability ellipsoids) of the chain structure of **1**. Both **1** and **2** feature the same chain topology.

ethyl acetate is hydrolyzed and then incorporated as acetate in the resulting structures.

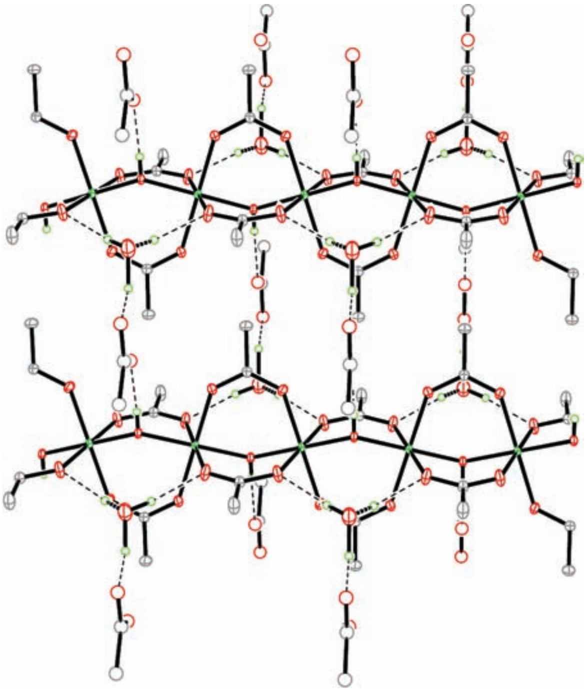

Figure 2. Depiction of the packing arrangement of **2** with hydrogen bonds shown. Methyl H atoms have been omitted. The acetic acid molecules are disordered over two positions related by a mirror plane; the average positions of these molecules are shown. The hydrogen bonding observed is similar to that in a reported manganese chain.[22]

These structures were discovered while investigating tridecameric group 13 hydroxo/aquo nanoclusters, such as the Ga_{13}, Al_{13}, and Ga_7In_6 compounds that we recently reported.[26−28] In attempting to isolate an analogous In_{13} structure (which has remained elusive), we instead produced the indium chain compound **1** (Figure 1).[29] The same methodology was then applied to isolate the gallium chain structure **2** (Figure 2). $M(NO_3)_3$ salts (M = Ga or In, 1 equiv) were dissolved in methanol, and *N*-nitrosopyrrolidine (1.85 equiv) was added, affording a yellow-tinted solution.[30] The solutions were evaporated open to air at room temperature, giving a viscous yellow solution. The vials were then sealed in jars containing ethyl acetate (~20 mL) to allow for vapor diffusion into the yellow solution. After several months, crystals suitable for single-crystal X-ray diffraction formed, revealing structures **1** and **2**, respectively. The indium compound was also isolated with di-*n*-butylnitrosamine in place of *N*-nitrosopyrrolidine. However, with $Ga(NO_3)_3$, this produced the previously reported Ga_{13} compound instead.[27] Interestingly, when the same conditions were applied to $Fe(NO_3)_3$, an iron trimer (well-known in the literature) was isolated instead of a chain structure.[31,32]

Structures **1** and **2** consist of an infinite linear chain of bridged metal ions (Figure 1).[33,34] Each trivalent octahedral metal ion is bound to two μ-OH groups and four μ-1,3-OAc ligands. These are shared with neighboring metal ions, giving a formula of $[M(\mu\text{-OH})(O_2CCH_3)_2]_n$, which results in an overall neutral charge. Interestingly, no interstitial molecules are present in **1**, and neighboring chain molecules show little intermolecular interaction. Many examples of group 13 carboxylate structures contain interstitial molecules, so it is unusual that chain structure **1** lacks such solvent molecules.[6,8,10−12,14,25]

Unlike the indium chain, the gallium chain contains acetic acid and water in the interstitial space between chains (Figure 2). As with the μ-1,3-OAc bridging ligands, acetic acid solvent is also derived from the hydrolysis of ethyl acetate. Acetic acid and water form a network of interchain hydrogen bonds throughout **2** (Figure 2). Acetic acid hydrogen-bonds to the hydroxyl bridges and water molecules, while the water molecules hydrogen-bond with the interstitial acetic acid and the O atoms of the acetate bridges. The acetic acid and water molecules in **2** are disordered over two positions related by a mirror plane. A similar network of hydrogen bonds, but without disorder, was found in the structure of the previously reported manganese chain.[22]

The presence of water and acetic acid in **2**, but not in **1**, can be rationalized in two ways. Gallium has a higher Lewis

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(29) The nitroso compound is vital to the formation of the M_{13} complexes that we have reported, which is why it was present in these reactions.

(30) HPLC-grade methanol was obtained from J. T. Baker and used without further purification (water content <0.1%). No attempt was made to keep the methanol anhydrous. Hydrated metal nitrate salts were also used, so all of the water available for incorporation as hydroxide bridges came from these salts, water in the solvent, and other adventitious water.

(31) The iron complex most similar to **1** and **2** that we have found is a linear trimer produced by Lippard and co-workers (Reisner, E.; Telser, J.; Lippard, S. J. *Inorg. Chem.* **2007**, *46*, 10754−10770).

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(33) Crystal data for **1**: $C_4H_7InO_5$, $M_r = 249.92$, colorless block, 0.34 × 0.18 × 0.09 mm, orthorhombic, space group *Cmcm*, $T = 173$ K, Mo Kα (0.717 03 Å), $a = 14.570(5)$ Å, $b = 6.831(2)$ Å, $c = 7.269(2)$ Å, $V = 723.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.294$ g/cm^3, $\mu = 3.23$ mm^{-1}, $F(000) = 480$, $2\theta_{max} = 56.5°$, 1962 reflections collected, 481unique [$R_{int} = 0.011$]. *R* indices [$I > 2\sigma(I)$]: R1 = 0.0167, wR2 = 0.0475, GOF = 1.131.

(34) Crystal data for **2**: $C_6H_{13}GaO_8$, $M_r = 282.88$, colorless block, 0.28 × 0.08 × 0.05 mm, monoclinic, space group *P*2(1)/*m*, $T = 173$ K, Mo Kα (0.717 03 Å), $a = 7.9516(7)$ Å, $b = 6.7651(6)$ Å, $c = 10.6719(10)$ Å, $\beta = 106.1500(10)°$, $V = 551.42(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.704$ g/cm^3, $\mu = 2.52$ mm^{-1}, $F(000) = 288$, $2\theta_{max} = 54.0°$, 6194 reflections collected, 1302 unique [$R_{int} = 0.024$]. *R* indices [$I > 2\sigma(I)$]: R1 = 0.0304, wR2 = 0.0782, GOF = 1.106.

acidity than indium and is therefore more likely to hydrolyze ethyl acetate, giving acetate or acetic acid. This may produce a higher acetate concentration in the crystallization solution. Gallium also has a smaller atomic radius than indium, which may leave more space in the crystal structure for the incorporation of interstitial water and acetic acid.

As mentioned, the origin of the acetate bridges, derived from the hydrolysis of ethyl acetate, is also of interest in these structures. Ethyl acetate is hydrolyzed and incorporated into the chain structures in two different ways: as bridging acetate ligands and as acetic acid in the interstitial spaces. Traditionally, extended structures bearing carboxylate ligands introduce the carboxylate moiety directly as, e.g., benzene carboxylates or sodium acetate. However, in a related example, Borovik and co-workers have described a case of mild ethyl acetate hydrolysis and acetonitrile hydration followed by structural incorporation of acetate and acetamidate ligands.[35] In this structure, the acetate moiety occupies a 1,3-bridging position between two Co^{II} ions while hydrogen-bonding with urea groups, similar to the binding motif seen in the gallium chain structure where acetate O atoms hydrogen-bond to water molecules. Borovik et al. were also able to isolate the same structure by direct treatment with an acetate source, whereas we have yet to isolate the chain structures by such means or in the absence of the nitroso compound.

The application of indium and gallium in organic transformations has been widely studied, with a range of transformation types examined, but reviews of the topic do not discuss hydrolysis reactions.[36-38] Nevertheless, these observations suggest that indium and gallium hydroxo complexes may be worth exploring as mild reagents for hydrolysis activation. For instance, in this report, up to three acetates are formed per metal ion based on the stoichiometry found in the crystals, and the crystallization vials also smell of acetic acid, providing further support of ester hydrolysis using group 13 metals.[39] Furthermore, it may be possible to use such an approach in the hydration of other molecules such as acetonitrile.

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Supporting Information Available: CIF files of single-crystal X-ray diffraction data (CCDC 716705 and 716706). This material is available free of charge via the Internet at http://pubs.acs.org.

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