Title

Stable Heterometallic Cluster Ions based on Werner's Hexol

Authors

Marsh, David A
Elliott, William S
Smith, Rachel M
et al.

Stable Heterometallic Cluster Ions based on Werner's Hexol

David A. Marsh, William S. Elliott, Rachel M. Smith, Meredith C. Sharps, Mary K. Baumeister, Matthew E. Carnes, Lev N. Zakharov, William H. Casey,* and Darren W. Johnson*

Abstract: *Large aqueous ions are interesting because they are useful in materials science (for example to generate thin films) but also because they serve as molecular models for the oxide–aqueous mineral interface where spectroscopy is difficult. Here we show that new clusters of the type $M[(\mu\text{-}OH)_2Co(NH_3)_4]_3$-$(NO_3)_6$ (M = Al, Ga) can be synthesized using Werner's century-old cluster as a substitutable framework. We substituted Group 13 metals into the hexol $Co[(\mu\text{-}OH)_2Co(NH_3)_4]_3^{6+}$ ion to make diamagnetic heterometallic ions. The solid-state structure of the hexol-type derivatives were determined by single-crystal XRD and NMR spectroscopy and confirmed that the solid-state structure persists in solution after dissolution into either D_2O or $[D_6]DMSO$. Other compositions besides these diamagnetic ions can undoubtedly be made using a similar approach, which considerably expands the number of stable aqueous heteronuclear ions.*

Nanoscale inorganic clusters have been shown to be useful precursors for solution processing of high-quality thin films.[1,2] Clusters are desirable precursors for thin films that can be included in devices and test structures due to their solubility in environmentally benign solvents, ease of deposition on surfaces, pre-organized structure, and lower temperatures of decomposition.[3] While various sol–gel based approaches satisfy these conditions, many use hybrid inorganic–organic mixtures that require large amounts of energy to process and have the potential to leave behind organic/carbon contaminants. Because of this, there is a need for precursors with minimal organic components that can be deposited from solution, to realize a low-energy and efficient method for producing thin films for a variety of applications.[4]

The well-known, venerable "Werner hexol" cluster (M = Co in Scheme 1) was originally synthesized in 1898 by
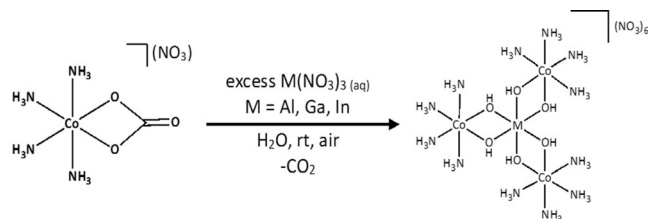
Scheme 1. Reaction between $[Co(NH_3)_4(CO_3)](NO_3)$ and metal nitrate salts to produce the hexol-type clusters, $M[(\mu\text{-}OH)_2Co(NH_3)_4]_3(NO_3)_6$.

Jörgensen,[5] and later studied by Alfred Werner to provide the first evidence for molecular chirality in the absence of carbon.[6,7] Later synthetic work by Kauffman and others developed methods to prepare additional salts and hydrates of this structure type.[7b] This cluster contained only cobalt ions and inorganic ligands such as hydroxide and ammine, and provided a wealth of information about coordination chemistry and the structure of inorganic molecules.[7] Importantly, this cluster—through its Δ and Λ twisted isomers—provided definitive proof that chirality was not solely the domain of organic molecules.

Despite spectacular examples of historically significant inorganic coordination clusters, the rational design of all-inorganic clusters can be challenging, with clusters often resulting from serendipity. This likely results from undesirable reactions (or precipitation) that produce the thermodynamically more stable bulk metal oxide/hydroxide.[8] It is for this reason that many successful strategies use organic ligands to suppress continued polymerization, resulting in elegant ligand-supported aqueous coordination clusters,[9] which are typically undesirable as materials precursors for reasons mentioned above. Methods have recently been developed for controlling these condensation reactions to allow for the synthesis and identification of clusters without stabilizing/supporting organic ligands, and provide a design strategy for preparing new clusters with different structures and new combinations of metal ions.[10–12] These approaches require delicate control over pH and hydrolysis.[13,14] We sought to use the acid-lability of carbonate ligands as a route to control condensation reactions, and we demonstrate this strategy by extending the hexol scaffold to incorporate other metal ions (Scheme 1). In this case, the acid is a Lewis-acidic Group 13 nitrate, and this method allows entry into new heterometallic derivatives of the Werner hexol.

Derivatives of the all-cobalt hexol cluster were synthesized through reactions of Group 13 metal nitrate salts with $[Co(NH_3)_4(CO_3)](NO_3)$ (Scheme 1). To produce the cluster containing aluminum, $Al[(\mu\text{-}OH)_2Co(NH_3)_4]_3(NO_3)_6$ (**CoAl**), an aqueous solution of $Al(NO_3)_3$ was added dropwise to an

[*] D. A. Marsh, W. S. Elliott, R. M. Smith, M. C. Sharps,
M. K. Baumeister, M. E. Carnes, D. W. Johnson
Department of Chemistry & Biochemistry and Materials Science
Institute, University of Oregon
Eugene, OR 97403-1253 (USA)
E-mail: dwj@uoregon.edu
Homepage: http://www.dwjlab.com/

L. N. Zakharov
CAMCOR, University of Oregon
1443 East 13th Ave., Eugene, OR 97403 (USA)

W. H. Casey
Department of Chemistry, Department of Earth and Planetary
Sciences, University of California, Davis
One Shields Ave, Davis, CA 95616 (USA)
E-mail: whcasey@ucdavis.edu

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201704073.

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aqueous solution of the carbonato precursor to achieve a Co:Al ratio of 1:1. Since a Co:Al ratio of 3:1 was required for the final product, an excess of aluminum was used to minimize formation of the all-cobalt cluster. In the low pH environment provided by the metal nitrate salt, carbonate ligands dissociate to produce CO_2 gas and create open coordination sites on Co.[15] In aqueous solution, a bis-aqua cobalt intermediate was formed that could undergo olation with the Group 13 metal aqua ions to form the hexol-type structure.[16] After allowing the reaction to proceed at room temperature, the desired product precipitated as a micro-crystalline solid that was purified by recrystallization from water. Using a metal nitrate salt to effect the dissociation of the carbonato ligand could also make this approach applicable to the incorporation of other metal ions, given the acidic nature of most metal nitrate salts. Although only Group 13 metal ions were tested here, it is thought that this approach could apply to any metal acidic enough to affect the dissociation of the carbonato ligand.

The data from single-crystal XRD shows that the aluminum analog adopts a similar structure as the original hexol cluster that contained only cobalt.[17,18] At the center is a six-coordinate Al^{3+} ion, bound with bridging hydroxide ligands that connect it to the outer $[Co(NH_3)_4]^{3+}$ units. The $-NH_3$ ligands are split into two chemical environments: either *cis* to bridging hydroxide ligands or *trans* to the hydroxide ligands, which can be distinguished in solution (see below). The overall charge on the cluster is balanced with six outer-sphere nitrate ions (Figure 1).

One advantage of preparing clusters with diamagnetic Co[III] and Al[III] ions is the use of ^{1}H-NMR and DOSY to understand their solution behavior. The spectrum obtained for the hexol-type clusters was surprisingly simple, which indicated that a pure species with high symmetry was present in solution. In [D6]DMSO only three resonances were observed and could be integrated to determine the ratio of protons (Figure 2). The two downfield resonances, at
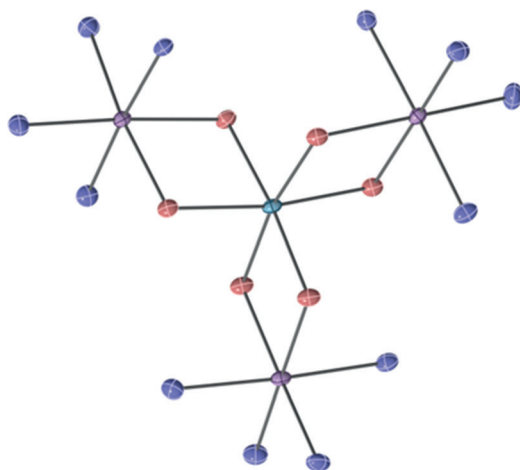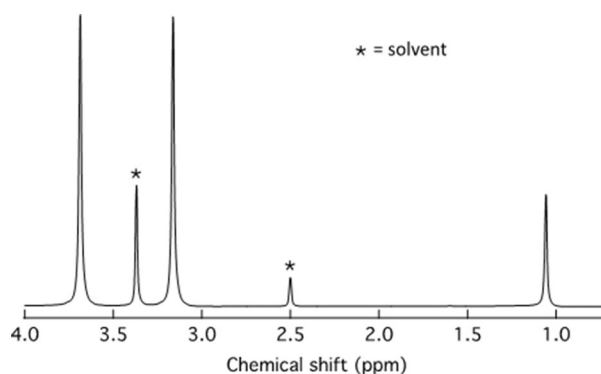

Figure 2. ^{1}H NMR of **CoAl** cluster in [D6]DMSO (residual solvent signals labeled with an *).

3.68 ppm and 3.15 ppm, both integrated to 18 protons, and the upfield resonance at 1.09 ppm represented 6 protons. Integration allowed for the assignment of the downfield signals to protons on the two types of ammine ligands (*cis* and *trans* to the hydroxide bridges) and the upfield signal was assigned to the bridging hydroxide protons. The spectrum obtained for **CoAl** had many similarities to what is observed for the all-cobalt hexol cluster,[17] showing that they adopt a similar structure in solution. Surprisingly, the same spectrum could be collected in D_2O with similar integration ratios to that in [D6]DMSO and confirmed the stability of the cluster at ca. 0.05 M concentrations in aqueous solutions (Figure S1 in the Supporting Information); over short-time periods (minute to hours) the **CoAl** cluster is resistant to both aqua ligand and proton/deuterium exchange.

Diffusion-ordered spectroscopy (DOSY) is an NMR technique to measure the diffusion coefficients of solutes. The hydrodynamic radii can then be estimated by the Stokes–Einstein relation. DOSY was collected to confirm that the three signals arose from protons on the same cluster, matching the solid-state structure, rather than three independent species (Figure 3). These data suggest the observed protons reside on the same cluster because the three resonances have the same diffusion coefficients, with an average of $8.5 \times 10^{-11} \pm 0.019\ m^2 s^{-1}$, indicating that all the protons were connected to a species diffusing through solution at the same rate. DOSY collected in D_2O also showed three resonances with the same diffusion coefficient, further confirming that this cluster is persistent in solution (Figure S2).

Solution state ^{27}Al NMR is a powerful technique used in defining the coordination environments of many aluminum species.[19,20] In addition to ^{1}H-NMR, ^{27}Al NMR was performed on $Al[(\mu-OH)_2Co(NH_3)_4]_3(NO_3)_6$ in [D6]DMSO (Figure 4). A single peak was observed in the spectrum at 36.6 ppm, arising from a six coordinate aluminum ion in solution that is much less shielded than the reference compound, $Al(H_2O)_6^{3+}$ (0 ppm). Four-coordinate aluminum ions give resonances further downfield, at 60 ppm or higher,[19] suggesting the peak at 36.6 ppm was in fact due to the aluminum ion observed at the center of the cluster in the solid-state structure. A single resonance is also good evidence that the cluster remains intact in solution, and that no other

Figure 1. Molecular structure of $Al[(\mu-OH)_2Co(NH_3)_4]_3^{6+}$ (**CoAl**). Thermal ellipsoids are shown at 50% probability, hydrogens omitted for clarity. The average Al−O, Co−O and Co−N bond lengths are 1.893-(10) Å, 1.908(9) Å, and 1.949(9) Å, respectively. Light blue = aluminum, purple = cobalt, red = oxygen, dark blue = nitrogen.
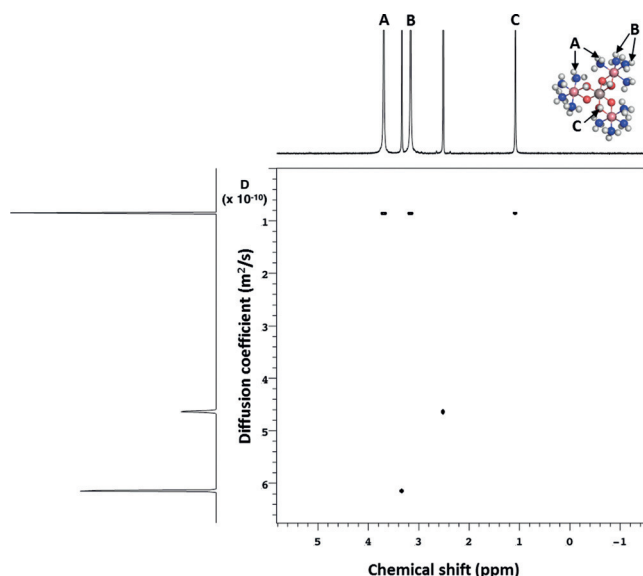
Figure 3. ^{1}H DOSY for CoAl cluster, showing the same diffusion coefficient for all protons not assigned to solvents.
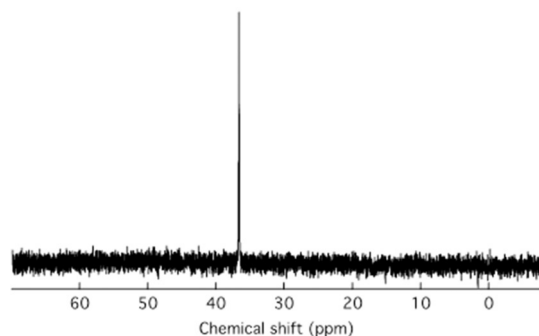

Figure 4. ^{27}Al NMR spectrum showing a single peak at 36.6 ppm.

aluminum-containing species were present, such as aluminum monomers (near 0 ppm).

To demonstrate that this approach applied to other metal ions, the gallium analog was synthesized using the same cobalt carbonato precursor and $Ga(NO_3)_3$ to acidify the solution. The cluster, **CoGa**, was isolated in a similar manner and found to be isostructural to the aluminum derivative in the solid state, based on single crystal XRD (Figure S3).[21] The NMR spectrum of **CoGa** was very similar to **CoAl**, indicating that the clusters with both aluminum and gallium were stable in solutions of [D$_6$]DMSO and D$_2$O (Figures S4 and S5). The diffusion coefficients measured by DOSY were only 5% different than those measured for the aluminum analog (Figures S6 and S7). The similarity in diffusion coefficient was reflected in their similar sizes measured crystallographically. The indium derivative was also prepared, but was always present as a mixture with the all-cobalt derivative using this method. Further purification was difficult and single crystals suitable for diffraction analysis could not be obtained. However, the ^{1}H NMR spectra again showed similar resonances to the analogs with aluminum and gallium, suggesting that the **CoIn** cluster was also present.

New heterometallic clusters have been synthesized based on Werner's hexol cluster with Group 13 metal ions, and have potential as precursors for aqueous solution deposition of thin films. Careful control over the metal composition in thin films is desirable, and this can be achieved through the synthesis of inorganic clusters and solution deposition processes. Using the synthetic method described here, other heterometallic derivatives of the hexol cluster might be attainable in the future to expand on the functionality of possible cluster species. This study shows that a new class of heteronuclear ions can be made based upon the hexol cluster of Werner. These clusters are not only useful in their own right, but such solutions can be hydrolyzed into useful thin films if the solutions are monospecific. We here focus on Group 13 metals, in part because the complexes are diamagnetic so that NMR signals could establish that they do not dissociate. However, a similar approach could greatly expand the library of clusters containing trivalent metals, including perhaps transition metals other than Co^{III}.

Conflict of interest

The authors declare no conflict of interest.

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[18] Crystallographic Data for **CoAl**: $Co_3H_{46.42}AlN_{18}O_{26.21}$, Al-$(OH)_6Co_3(NH_3)_{12}(NO_3)_6(H_2O)_{2.21}$, $M = 922.08$, $0.22 \times 0.17 \times 0.08$ mm, $T = 100$ K, orthorhombic, space group *Pbca*, $a = 16.895(2)$, $b = 17.120(3)$, $c = 22.173(3)$ Å, $V = 6413.2(16)$ Å^3, $Z = 8$, $\rho_{cald} = 1.910$ Mg m^{-3}, $\mu(Mo) = 1.683$ mm^{-1}, $F(000) = 3809$, $2\theta_{max} = 54.0°$, 60136 reflections, 7005 independent reflections [$R_{int} = 0.0241$], $R1 = 0.0262$, $wR2 = 0.0657$ and GOF $= 1.022$ for 7005 reflections (629 parameters) with $I > 2\sigma(I)$, $R1 = 0.0332$, $wR2 = -0.710$ and GOF $= 1.022$ for all reflections, max/min residual electron density $+0.830/-0.464$ e Å^{-3}. CCDC 1493597 (**CoAl**) and 1493598 (**CoGa**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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[21] Crystallographic data for **CoGa**: $Co_3H_{46.5}GaN_{18}O_{26.25}$, Ga-$(OH)_6Co_3(NH_3)_{12}(NO_3)_6(H_2O)_{2.25}$, $M = 965.56$, $0.20 \times 0.15 \times 0.14$ mm, $T = 173$ K, triclinic, space group $P\bar{1}$, $a = 12.0845(9)$, $b = 12.4798(9)$, $c = 12.5484(8)$ Å, $\alpha = 61.953(3)$, $\beta = 81.612(4)$, $\gamma = 82.833(4)°$, $V = 1648.9(2)$ Å^3, $Z = 2$, $\rho_{cald} = 1.945$ Mg m^{-3}, $\mu(Mo) = 2.409$ mm^{-1}, $F(000) = 989$, $2\theta_{max} = 65.96°$, 40797 reflections, 12212 independent reflections [$R_{int} = 0.0931$], $R1 = 0.0463$, $wR2 = 0.0698$ and GOF $= 1.003$ for 12212 reflections (625 parameters) with $I > 2\sigma(I)$, $R1 = 0.0843$, $wR2 = 0.0970$ and GOF $= 1.003$ for all reflections, max/min residual electron density $+0.812/-0.767$ e Å^{-3}.