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Title

A Re-examination of the Synthesis of Monolayer-Protected Co_x (SCH₂CH₂Ph)_m Nanoclusters: Unexpected Formation of a Thiolate-Protected Co(II) T₃ Supertetrahedron

Permalink

<https://escholarship.org/uc/item/1ft62691>

Journal

Inorganic Chemistry, 57(14)

ISSN

0020-1669

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Publication Date

2018-07-16

DOI

10.1021/acs.inorgchem.8b00672

Peer reviewed

a D₂O solution of NaBH₄ (9 equiv) we observe a color change to dark green. This solution then slowly turned dark brown, concomitant with the deposition of a grey-brown solid. A ¹H NMR spectrum of the reaction mixture after 30 min reveals the presence of three diagnostic resonances at -10.02, 103.22, and 120.11 ppm (Figure S4), which are assignable to the cobalt(II)-thiolate cluster, [Co₁₀(SR)₁₆Cl₄] (**1**) (see below). Complex **1** is the only major product observed in the reaction mixture, demonstrating that the transformation is remarkably chemoselective.

To facilitate the isolation of **1** we repeated the above procedure in the absence of water and in an inert atmosphere glove box (Scheme 2). Work-up of this reaction mixture results in the isolation of dark brown crystals of the cobalt-thiolate cluster [Co₁₀(SR)₁₆Cl₄] (**1**) in 37% yield. Also formed in this reaction is a grey-brown solid, whose appearance is consistent with that of NaCl, but which is contaminated with small amounts of a Co-containing product. We believe the modest yield of this reaction is due to the presence of excess thiol (see below), which impedes the crystallization process.

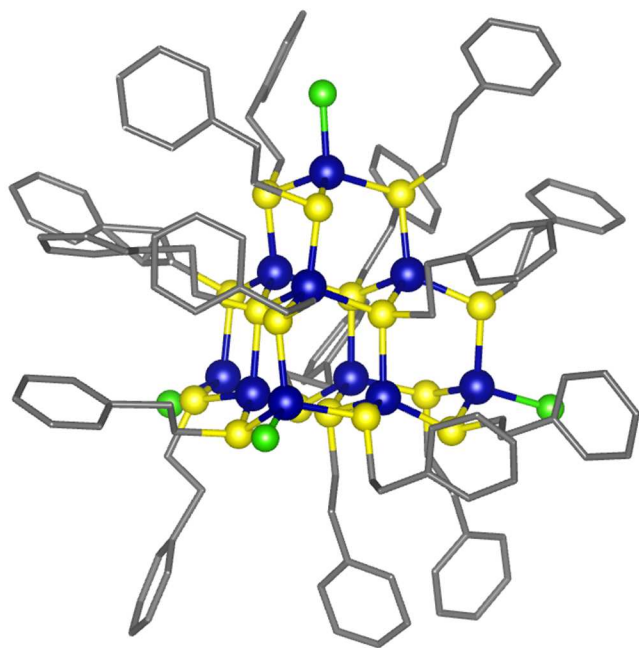


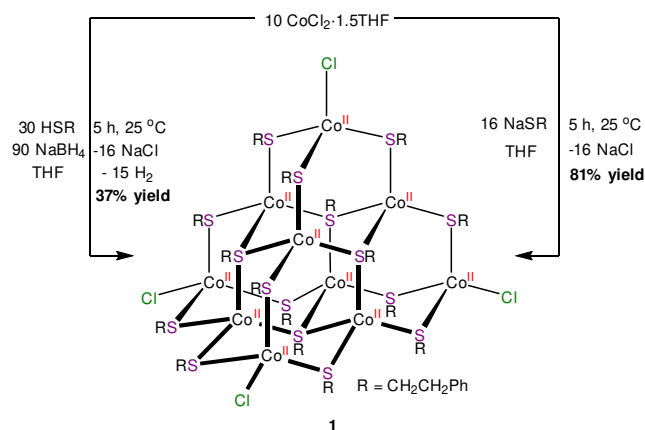
Figure 1. Ball-and-stick diagram showing **1**·2CH₂Cl₂. Hydrogen atoms and CH₂Cl₂ solvate molecules omitted for clarity. Color legend: Co = blue; S = yellow; C = grey; Cl = green

Complex **1** crystallizes in the monoclinic space group *Cc* as the CH₂Cl₂ solvate, **1**·2CH₂Cl₂ (Figure 1). It features a [Co₆S₁₆Cl₄] core with idealized T_d symmetry. Each of the ten Co centers features a pseudo-tetrahedral geometry and the four Cl⁻ ligands occupy the corners of the tetrahedron. Twelve of the 16 thiolate ligands feature a μ₂ binding mode. These are situated along the edges of the tetrahedron in six groups of two. Four of the thiolate ligands feature a μ₃ binding mode. These are situated at the centers of each triangular face. The average Co-Cl distance is 2.21 Å, which is consistent with the values reported for the related cluster, [NBu₄]₂[Co₄(SPh)₆Cl₄].⁵³ Similarly, the Co-S distances for the μ₂ thiolate ligands (range: 2.24-2.32 Å) are within the reported range for the related Co thiolate clusters, [NBu₄]₂[Co₄(SPh)₆Cl₄] and M₂[Co₄(SPh)₁₀] (M = Me₄N⁺, Et₄N⁺, hexyl₂NH₂⁺).⁵³⁻⁵⁴ The Co-S distances for the μ₃ thiolate

ligands (range: 2.30-2.35 Å) are generally longer, but overlap somewhat with those observed for the μ₂ thiolate ligands. Finally, the long Co-Co distances (range: 3.66-3.97 Å) in **1** precludes the presence of any direct Co-Co bonds. Similar Co-Co distances were also observed for [NBu₄]₂[Co₄(SPh)₆Cl₄] and M₂[Co₄(SPh)₁₀].⁵³⁻⁵⁴

Complex **1** is a rare example of an open-shell, chalcogenide-stabilized T₃ supertetrahedral cluster.⁵⁵⁻⁵⁶ Comparable chalcogenide-stabilized supertetrahedra, such as [Cd₁₀(SCH₂CH₂OH)₁₆][X]₄ (X = ClO₄⁻, NO₃⁻, SO₄²⁻)⁵⁷⁻⁵⁹ and [Me₄N]₂[E₂M₁₀(SPh)₁₆] (E = S, Se; M = Zn, Cd),⁶⁰ feature the diamagnetic Zn²⁺ and Cd²⁺ ions. Other open-shell supertetrahedra, such as [M₁₀O(tmp)₄(diketonate)₄] (M = Ni, Co; H₃tmp = 1,1,1-tris(hydroxymethyl)propane) and [Mn₁₀O₄(N₃)₄(hmp)₁₂][ClO₄]₂ (Hhmp = 2-(hydroxymethyl)pyridine) feature alkoxide co-ligands.⁶¹⁻⁶³ Complex **1** can also be viewed as the T₃ analogue of known T₂ supertetrahedral clusters, M₂[Co₄(SPh)₁₀] (M = (Me₄N⁺, Et₄N⁺, hexyl₂NH₂⁺) and [NBu₄]₂[Co₄(SPh)₆Cl₄],⁵³⁻⁵⁴ which are themselves closely related to the classic monometallic cobalt-thiolate complexes, M₂[Co(SPh)₄] (M = PPh₄⁺, Et₄N⁺).⁶⁴⁻⁶⁵

Scheme 2. Syntheses of **1**



We next endeavored to synthesize complex **1** via a rational route (Scheme 2). Given that NaBH₄ appears to be acting solely as a base during the formation of **1**, we rationalized that the reaction protocol could be simplified by substitution of PhCH₂CH₂SH/NaBH₄ with NaSCH₂CH₂Ph. Thus, reaction of CoCl₂·1.5THF with 1.6 equiv of NaSCH₂CH₂Ph in THF resulted in the formation of a green solution, which gradually turned dark brown over the course of 5 h, concomitant with the deposition of a grey powder. Work-up of the reaction mixture allowed for the isolation of **1** as a dark brown crystalline solid. When synthesized in this fashion complex **1** can be isolated in 81% yield.

A ¹H NMR spectrum of **1** in CD₂Cl₂ features 10 resonances, ranging from 115.7 to -19.6 ppm. The number of resonances, and their integrations, are consistent with the presence of two magnetically inequivalent thiolate environments in a 12:4 ratio, as predicted by the solid-state molecular structure. More significantly, the resonances at 115.7, 57.2, and -19.6 ppm feature very similar chemical shifts to the diagnostic resonances observed in the ¹H NMR spectrum of the *in situ* reaction mixture (see above). This further confirms that **1** is being formed in the reaction of CoCl₂ with PhCH₂CH₂SH and NaBH₄ in THF/H₂O. The electrospray ionization (ESI) mass spectrum of complex **1** in CH₂Cl₂, acquired in negative ion

mode, is also consistent with our proposed formulation (Figure 2). The major feature at $m/z = 2929.9475$ is assignable to two overlapping ions: the parent peak $[M]^-$ and the fragment $[Co_9(SR)_{16}Cl_4 + Cu]^-$. Additionally, a peak at $m/z = 2962.9119$ is assignable to $[M + Cl]^-$.

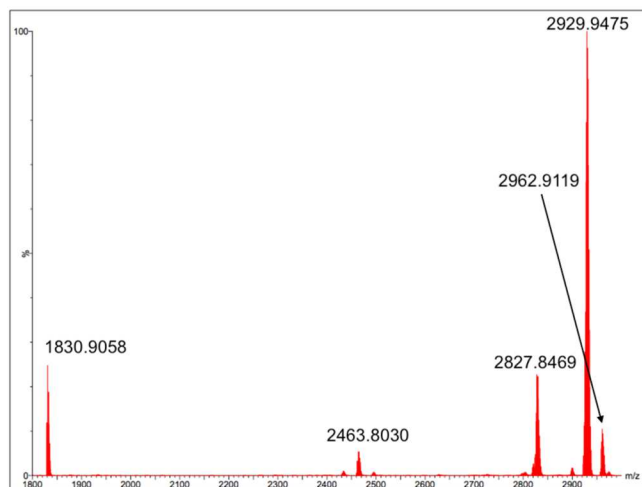


Figure 2. ESI-MS of complex **1** in negative ion mode.

Magnetic susceptibility data were also collected on a microcrystalline sample of **1** (Figure 3). At 300 K, complex **1** exhibits an effective magnetic moment of 7.36 B.M., lower than the anticipated spin-only effective magnetic moment (12.25 B.M.), and indicative of moderate antiferromagnetic coupling between cobalt centers. Dance also reported antiferromagnetic coupling between the Co centers in $[NMe_4]_2[Co_4(SPh)_{10}]$ (average $J = -17 \text{ cm}^{-1}$).⁵⁴ Finally, the magnetization curve M vs. H is linear, implying that complex **1** is a simple paramagnet (Figure 3), and shows no hysteresis at any temperature.

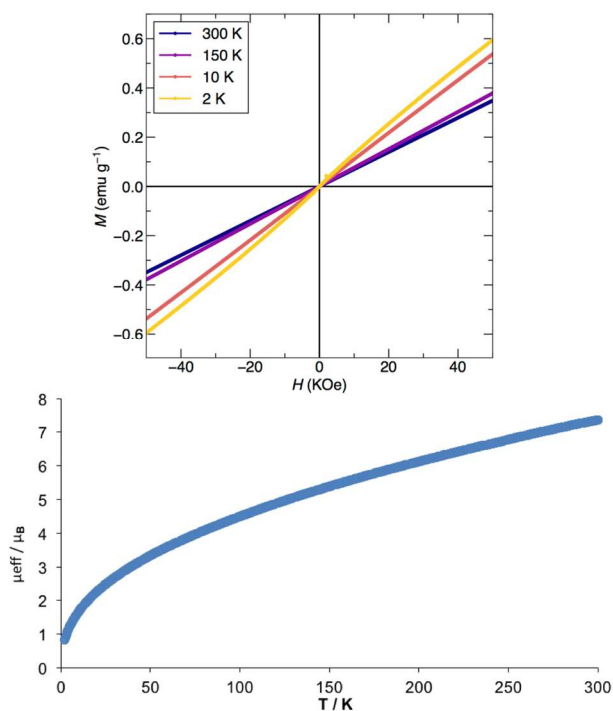


Figure 3. Solid-state magnetic susceptibility data M vs. H (top) and μ_{eff} vs. T (bottom) for **1** measured from 2 to 300 K.

We also endeavored to examine the effect of reaction stoichiometry on the formation of **1**. The reaction of $CoCl_2 \cdot 1.5THF$ with 1 equiv of NaSR still results in the formation of **1**, but with a significantly reduced yield (ca. 16%). Similarly, reaction of $CoCl_2 \cdot 1.5THF$ with 2 equiv of NaSR (Figure S7) resulted in the formation of large number of paramagnetic, Co-containing products, including complex **1** (but in insignificant amounts). Not surprisingly, we were unsuccessful in our attempts to isolate any products from this reaction mixture. From these experiments, we hypothesize that Cl^- must play an important role in directing the self-assembly of **1**. Presumably, the use of greater than 1.6 equiv of thiolate per Co results in a deficiency of Cl^- , which prevents the assembly of **1** and results in formation of a broad distribution of clusters. Previous workers have also noticed that the speciation of Co(II)-thiolates is highly dependent on reaction stoichiometry.⁵³⁻⁵⁴

We also briefly examined the chemical properties of complex **1**. It is soluble in benzene, toluene, and CH_2Cl_2 , but insoluble in MeCN, Et_2O , and alkanes. Complex **1** is soluble in THF, but partially decomposes over the course of 5 h, as evidenced by the deposition of a brown solid on standing in this solvent (Figure S6). Attempted dissolution of **1** in $py-d_5$ results in immediate formation of a green solution that contains no resonances assignable to **1**, concomitant with deposition of a brown solid (Figure S8). While **1** clearly reacts with pyridine, we have been unable to determine the identity of the product(s) formed.

The reaction of $CoCl_2$ by $NaBH_4$, both in the presence or absence of a passivating ligand, has been studied extensively.^{49-50, 66-70} In the absence of a passivating ligand, these reductions result in the formation of finely-divided Co(0) (in non-aqueous solvents) or Co_2B (under aqueous conditions).⁶⁶ In the presence of a passivating ligand, or in the presence of surfactant, the results are more complicated. In one instance, this reaction resulted in the formation of simple Co(II) thiolate complexes,⁶⁹⁻⁷⁰ while in other cases authentic Co(0) nanoparticles were generated.^{49-50, 66-68} Given this past precedent, as well as our own experiments, we believe that the 2017 synthesis initially resulted in formation of **1**, and not $Co_x(SCH_2CH_2Ph)_m$ -type nanoclusters, as originally suggested. However, complex **1** then decomposed upon exposure to air and water during work-up, likely generating a mixture of $Co_xO_y(SCH_2CH_2Ph)_m$ -type clusters. Consistent with this hypothesis, exposure of complex **1** to air, as a CH_2Cl_2 solution, results in a color change from deep brown to coral. A UV-vis spectrum of this solution features absorptions at 404, 493, and 611 nm (Figure S19). These values are very similar to those reported in 2017 for $Co_x(SCH_2CH_2Ph)_m$, demonstrating that the original material requires O_2 for its formation, and is therefore unlikely to contain any Co(0) character.

Conclusion

We have re-examined the synthesis of thiolate-protected cobalt APNCs by reaction of $CoCl_2$ with $NaBH_4$ and $PhCH_2CH_2SH$. Despite efforts to faithfully reproduce the reported procedure, we are unable to detect the presence of a cobalt(0)-containing APNC. Instead, we isolated the intriguing Co(II) cluster, $[Co_{10}(SR)_{16}Cl_4]$. This complex represents the first example of a thiolate-protected Co(II) T3 supertetrahedron. We believe that $[Co_{10}(SR)_{16}Cl_4]$ was also being formed in the original synthesis; however, the cluster likely reacted with oxygen and water during work-up, giving a mix of

Co_xO_y(SCH₂CH₂Ph)_m-type clusters. This result highlights the challenges inherent in the generation of low-valent cobalt nanoclusters, including the need for rigorous exclusion of air during their synthesis, work-up, and characterization.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

X-ray data for compound **1**·2CH₂Cl₂ (CIF)

Experimental procedures, crystallographic details, and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the National Science Foundation (CHE 1361654) for financial support. NMR spectra were collected on an instrument supported by an NIH Shared Instrumentation Grant (SIG, 1S10OD012077-01A1). ESI mass spectra were acquired at the MRL Shared Experimental Facilities, supported by the MRSEC Program of the NSF under Award No. DMR 1720256 and a member of the NSF-funded Materials Research Facilities Network. A. W. C. thanks the Mellichamp Academic Initiative in Sustainability at UCSB for a summer fellowship. We also thank Joshua Bocarsly for his assistance in the collection and interpretation of the magnetism data.

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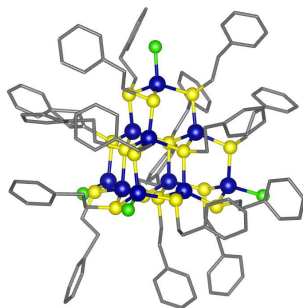
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Reaction of CoCl_2 with NaBH_4 and $\text{HSCH}_2\text{CH}_2\text{Ph}$, in THF, results in formation of $[\text{Co}_{10}(\text{SCH}_2\text{CH}_2\text{Ph})_{16}\text{Cl}_4]$. This complex represents the first example of a thiolate-protected Co(II) T3 supertetrahedron.
