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Synthesis and Characterization of a High-Nuclearity Cluster with a (μ_4-Oxo)tetracobalt(II) Core

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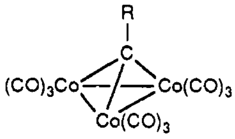
Summary: Addition of the solution obtained from reaction of $AlCl_3$ and $ClCCo_3(CO)_9$ in CH_2Cl_2 to ice water gives high yields of $OCo_4[O_2CCCo_3(CO)_9]_6$ as a brick red crystalline solid. Structural characterization reveals a distorted-tetrahedral OCo_4 core with each of the six edges bridged by a (carboxymethylidyne)tricobalt nonacarbonyl group. Treatment with concentrated H_2SO_4 and addition of the solution thus formed to water returns the intact cluster, but addition of the H_2SO_4 solution to methanol results in fragmentation to $CH_3O_2CCCo_3(CO)_9$.

We report herein the isolation and characterization (chemical and structural) of a remarkable polycarboxylate cluster built about a tetrahedral (μ_4-oxo)tetracobalt core. This compound was obtained by an unexpected spontaneous self-assembly process that bears on the ill-defined mechanism of CO migration to form acylium ions of methylidynetricobalt nonacarbonyl. It is additionally a molecule of some aesthetic interest in light of recent reports regarding similar molecules of high symmetry and pleasing geometric appearance.[1,2]

We are interested in interactions, particularly of an intramolecular nature, of olefin moieties with derivatives of methylidynetricobalt nonacarbonyl (1). To this end, we required the allyl ester 2, first prepared by Seyferth[3] in the 1970s. The ester is readily obtained from the chloro derivative 3 upon reaction with a 3-fold excess of $AlCl_3$ in CH_2Cl_2, followed by addition of excess allyl alcohol and washing with 10% HCl. However, an attempt with a stoichiometric rather than an excess amount of alcohol gave instead a brick red solid upon aqueous workup, which dissolved only with difficulty in benzene and polar organic solvents such as alcohols and THF. We then found that neither the allyl alcohol nor the acid was necessary to obtain this substance. Thus, reaction of 3 with $AlCl_3$ in CH_2Cl_2 gave a yellow-brown solution after $^1/_2$ h. This solution was poured directly over cracked ice, affording the same brick red, crystalline solid in 84% yield based on total cobalt.[4]



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2, R = $COOCH_2CHCH_2$
3, R = Cl
5, R = $COOCH_3$
6, R = COOH

Table I. Crystallographic Data for 4

compd	$Co_{22}C_{66}O_{67}\cdot 2C_6H_{14}$	Z	3
fw	3333.6	λ, Å	0.710 69
space group	$R\bar{3}$ (No. 148)	ρ_{calcd}, g/cm^3	1.66
a, Å	16.256 (2)	μ(Mo Kα), cm^{-1}	31.7
c, Å	37.70 (9)	transmissn coeff	0.45–0.58
V, Å^3	8621 (6)	R, %	6.72
T, K	130	R_w, %	5.92

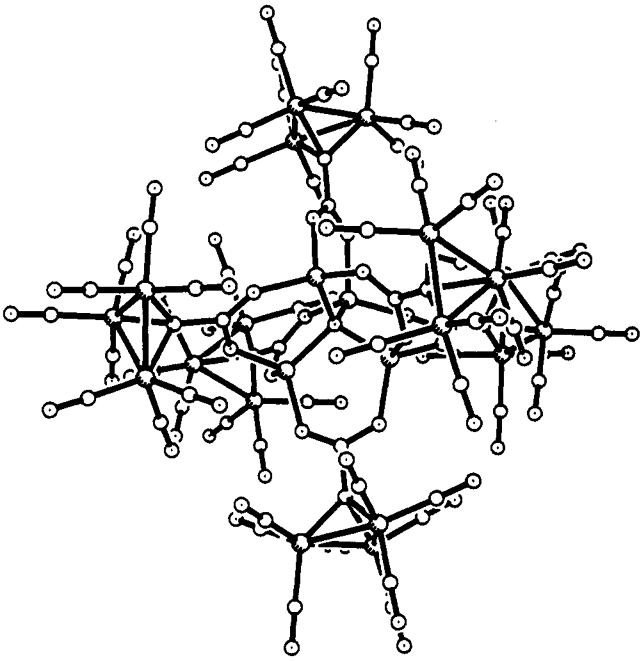

Figure 1. Computer-generated drawing of 4, with disorder removed. In all drawings (except where noted) oxygens are dotted, cobalts are shaded, and carbons are plain.

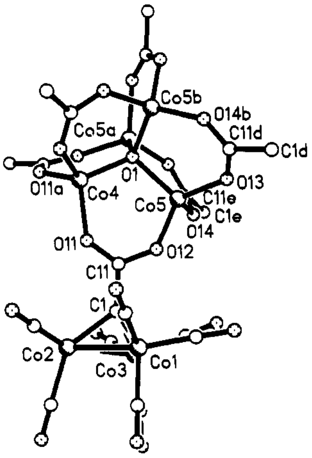

Figure 2. Computer-generated drawing of 4, with disorder and five of the methylidynetricobalt nonacarbonyl units removed for clarity. Important bond distances and angles are given in Table II.

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(1) E.g., for leading references on "fullerene" see: (a) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. (b) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983. (c) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167. See also the "molecular ferric wheel" in: Taft, K. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 9629.

(2) Sturgeon, R. L.; Schore, N. E.; Olmstead, M. M. *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, Aug 1990; American Chemical Society: Washington, DC, 1990; INOR 63.

(3) (a) Seyferth, D.; Hallgren, J. E.; Eschbach, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 1730. (b) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (c) Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 758.

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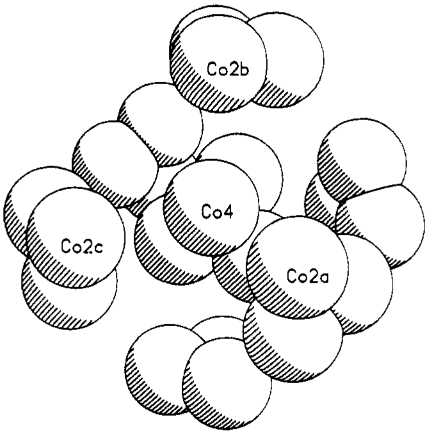

Figure 3. Computer-generated drawing of 4 showing only the cobalts.

Table II. Selected Bond Lengths and Angles

	Bond Lengths		
Co(4)–O(1)	1.905 (5)	Co(5)–O(1)	1.966 (4)
Co(4)–O(11)	1.96 (2)	Co(5)–O(11)	1.93 (1)
Co(5)–O(13)	1.94 (2)	Co(5)–O(14)	1.95 (1)
C(11)–O(11)	1.26 (2)	C(11)–O(12)	1.23 (2)
C(11d)–O(13)	1.29 (2)	C(11e)–O(14)	1.22 (2)
C(1)–C(11)	1.50 (2)	Co(1)–Co(2)	2.480 (2)
Co(1)–Co(2)	2.481 (2)	Co(2)–Co(3)	2.470 (3)
C(1)–Co(1)	1.87 (1)	C(1)–Co(2)	1.88 (2)
C(1)–Co(3)	1.88 (2)		
	Nonbonded Lengths		
Co(4)–Co(5)	3.207	Co(5)–Co(5a)	3.162
	Bond Angles		
Co(4)–O(1)–Co(5)	111.9 (1)	Co(5)–O(1)–Co5(a)	107.0 (1)
O(1)–Co(4)–O(11)	108.9 (4)	O(1)–Co(5)–O(13)	111.4 (7)
O(1)–Co(5)–O(13)	107.4 (5)	O(1)–Co(5)–O(14)	112.1 (4)
O(11)–Co(4)–O(11a)	110.0 (5)	O(12)–Co(5)–O(13)	106.6 (6)
O(13)–Co(5)–O(14)	110.9 (6)	O(12)–Co(5)–O(14)	108.1 (8)
Co(4)–O(11)–C(11)	134 (1)	Co(5)–O(12)–C(11)	133 (1)
Co(5)–O(13)–C(11d)	129 (1)	Co(5)–O(14)–C(11e)	127 (1)
O(11)–C(11)–O(12)	121 (2)	O(13)–C(11d)–O(14b)	129 (2)
C(1)–C(11)–O(11)	125 (1)	C(1)–C(11)–O(12)	115 (1)
C(1d)–C(11d)–O(13)	114 (1)	C(1e)–C(11e)–O(14)	117 (1)

This material remains unchanged upon heating above 300 °C. It shows no ^{1}H NMR resonances (benzene-d_6), while ^{13}C NMR spectroscopy shows a small resonance at 195 ppm and a broad (ca. 5000 Hz wide) feature centered at 110 ppm. In the IR spectrum (KBr) bands at 1642, 2005, 2020, 2033, 2049, and 2111 cm^{-1} are present, similar to those seen for other substituted 1-derived clusters. The ESR spectrum (CH$_3$CN glass, 10 K) shows a broad featureless peak at $g = 4.0$, indicative of the presence of Co(II); the system is antiferromagnetic with $\mu_{\mathrm{eff}} = 4.75\ \mu_{\mathrm{B}}$ and $\Theta = -27\ (3)$ K.[5]

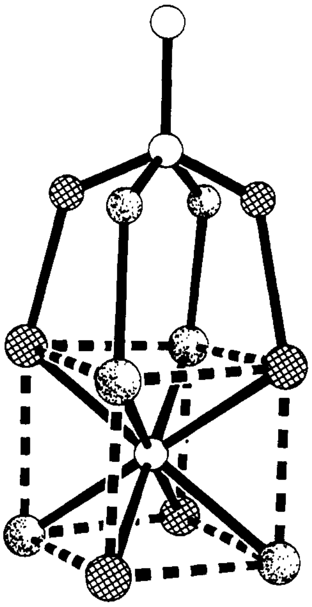

Figure 4. Computer generated drawing of 4 including disorder, with all the methylidynetricobalt nonacarbonyl units and five carboxylates removed for clarity. The dotted and the cross-hatched atoms are each at half-occupancy and represent two different molecules, while the plain atoms are at full occupancy.

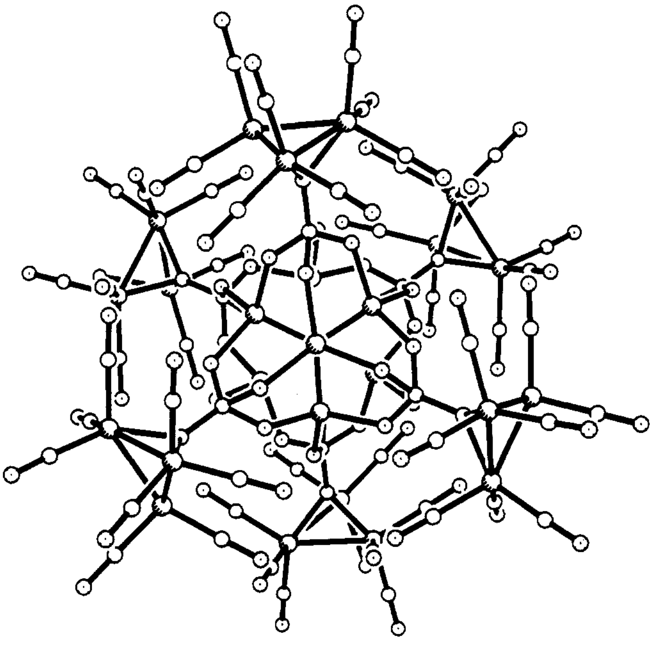

Figure 5. Computer-generated drawing of 4 including disorder, viewed along the *c* axis.

After considerable effort, single-crystal X-ray-diffraction-quality crystals were grown by crystallization by slow diffusion of hexane into benzene. The crystallographic data are summarized in Table I. As shown in Figures 1 and 2, the compound (4) has a tetrahedral oxygen coordinated to four cobalt atoms. Six tricobalt-cluster-derived carboxylates bridge the edges of the tetrahedron, giving the overall formulation of OCo$_4$[O$_2$CCCo$_3$(CO)$_9$]$_6$. Charge balance is satisfied with four Co(II) and a central O^{2-} atom. Each of the central cobalt(II) atoms is tetrahedral, coordinated to four oxygens: the central oxide and three from carboxylates. Co(4) is unique, sitting on a 3-fold axis, with a shortened bond to O(1); its geometry is closest to tetrahedral. Co(5a) and Co(5b) are symmetry-generated from Co(5). Figure 3 shows a space-filling representation of just the Co atoms. Each of the three Co$_3$ triangles orients toward Co(4) to give one short (Co(4)–Co(2a) = 5.335 Å) and two nearly equal long (Co(4)–Co(1a) = 5.872 Å and Co(4)–Co(3a) = 5.832 Å) nonbonding distances, while the orientation of the three nearest Co$_3$ triangles toward each Co(5) atom gives one short, one intermediate, and one long nonbonding distance for each. Table II gives selected bond

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(4) Experimental details: 5.645 g (42.35 mmol) of AlCl$_3$ was added to a solution of 5.139 g (10.79 mmol) of 3 in CH$_2$Cl$_2$. After 30 min the solution was poured over cracked ice. The brick red solid obtained after filtering the warmed mixture was washed with copious amounts of water and dried under vacuum to afford 3.892 g (1.231 mmol) of 4 (84% yield based on available Co from 3).

(5) $C = 2.82\ (8)$ and $\chi_0 = 0.0029\ (2)$.

lengths and angles; the **1**-derived carboxylates are essentially the same as those previously published.[6] The space group requires $\bar{3}$ point symmetry for the molecule; thus, there is a statistical disorder of the central cobalt tetrahedron which gives the appearance of an oxygen at the center of a distorted cube with a cobalt of half-occupancy at each corner. One carboxylate spans each face of the cube; thus, the disorder is accommodated simply by rotating the COO units from one face diagonal of the cube to another (Figure 4). The outside of the cluster (Figure 5) appears rather like a slightly flattened sphere and packs as such with random orientation of the central tetrahedron. An attempt to solve the structure in a lower symmetry space group ($R3$) to relieve the disorder was unsuccessful. The structure reveals two disordered hexane molecules per cluster. The elemental analysis on the dried material indicates loss of some of the hexane.[7] Crystals from a second synthesis possessed the same space group but different cell parameters due to incorporation of only one molecule of solvent. Refinement of this structure was inferior to the one reported here.[8]

Although cluster **4** was unreactive toward dilute acids, it dissolved in concentrated H_2SO_4 to give a yellow-brown solution, which was initially thought to be Seyferth's **1**-derived acylium ion (i.e., $R = -C{\equiv}O^+$).[3,9] However, when this solution was poured over cracked ice, a 95% recovery of **4** was realized. When the solution was poured into ice-cold methanol and allowed to stand overnight, **4** was quantitatively converted to methyl ester **5**. This ester was converted to the corresponding acid **6** when dissolved in concentrated sulfuric acid and poured over cracked ice. On the other hand, **4** was very soluble in dry methanol but remained unchanged after several days in solution. Addition of concentrated H_2SO_4 converted only a fraction of **4** to **5** after 24 h. The cluster is stable in benzene for extended periods but decomposes slowly in acetonitrile.

The preparation of **4** gives clues about the reaction of halo-**1** (e.g., **3**) with Lewis acids such as $AlCl_3$. Seyferth showed that although **3** must gain a carbonyl in forming the acylium ion, saturating the solution with free CO did not appreciably affect the yield; i.e., unsaturated species resulting from CO migration prefer to cannibalize CO from other clusters rather than pick up free CO from solution. The presence of four Co(II) atoms in **4** requires that coordinatively unsaturated cobalt from cannibalized clusters remain in soluble form, susceptible to rapid formation of some undefined hydrated species upon aqueous workup, which may then condense directly with **1**-derived acylium ions en route to **4**. In syntheses of **1**-derived esters, e.g. **2** or **5**, these cobalts are presumably trapped initially as alkoxy species which are unable to react with the acylium ions. We assume (without direct evidence) that the extra oxygens of the carboxylates as well as of the oxide in the center of **4** are all water-derived. Neither the timing nor the details of the oxidation to Co(II) are known at this time. It is also not clear when or how the central OCo_4^{6+} core is assembled. The resistance of the cluster to nucleophilic attack is quite extraordinary, attesting to the degree of protection provided by the six hindered carboxylates.

μ_3-Oxo carboxylate clusters of many transition metals[10] have attracted attention recently, particularly those of Co(III), because they are thought to be intimately involved in catalytic oxidation processes.[11] They are well-characterized and are formed under mild conditions. However, μ_4-oxo clusters of Co(II) carboxylates are rare, although mass spectrometry evidence suggests that the structure of **4** is the preferred structure of cobalt carboxylates in the gas phase.[12] To our knowledge, the most fully characterized example in the condensed phase is a form of cobalt pivalate obtained by vacuum pyrolysis at 220–230 °C.[13] In contrast, cluster **4** is formed rapidly in nearly quantitative yield at room temperature in the presence of water and oxygen (under highly acidic conditions as well). The formation of the tetrahedral (μ_4-oxo)tetracobalt cluster would appear to be quite favorable; the lack of earlier examples probably arises from its lability in the absence of protecting ligands. The peripheral **1**-derived moieties dominate the spectroscopy and redox chemistry of **4**. For instance, oxidation of **4** with $AgNO_3$ disrupts the cluster, obscuring possible oxidation of the central Co(II) to Co(III), which might lead to Sumner's μ_3-oxo clusters and provide a link to catalytic oxidation processes. We are seeking ways to make other μ_4-oxo clusters with sterically hindered carboxylates for further study of these intriguing systems.

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Supplementary Material Available: A plot of the temperature dependence of the magnetic susceptibility and tables of complete crystallographic data, atomic coordinates, thermal parameters, bond lengths, and bond angles for **4** (7 pages); a listing of observed and calculated structure factors for **4** (11 pages). Ordering information is given on any current masthead page.

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(7) Anal. Calcd for $Co_{22}C_{66}O_{67}\cdot 1.33C_6H_{14}$: Co, 39.57; C, 27.13. Found: Co, 39.13; C, 26.85.

(8) $Co_{22}C_{66}O_{67}$ crystallizes in the hexagonal space group $R\bar{3}$ with a = 15.302 (3) Å, c = 41.157 (9) Å, V = 8346 (6) Å^3, and Z = 3.

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