We are continuing our studies on the synthesis and structural analysis of E-selectin related oligosaccharides and will report on our results in due course.

Supplementary Material Available: Details of the experimental procedures for the synthesis of the β-O-allyl glycosides and compounds 1 and 2 and spectral data for 1 and 2 (28 pages). Ordering information is given on any current masthead page.

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On the Interface of Metal–Metal Multiple Bond Compounds and Organometallic Clusters: Synthesis and Structure of Mo2{μ-[(CO)9Co3(μ3-CCO2)]}4[(CO)9Co3(μ3-CCO2H)]2 and Related Compounds

W. Cen, P. Lindenfeld, and T. P. Fehlner*

Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, Indiana 46556
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The octahedral array of organometallic clusters in M^{II}_4-$[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$, M = Zn, Co,[1-3] is defined by the tetrahedral M^{II}_4 core (Scheme Ia). In order to explore the consequences of a square planar geometry (Scheme Ib), we have now investigated metal–metal quadruply bonded compounds[4-6] as cores for coordinating organometallic cluster carboxylate ligands.[7] Although some related chemistry is known,[5,8] hybrid compounds having both quadruply bonded and trimetal alkylidyne subunits are not. Another development is the assembly of metal–metal multiple bond compounds into low-dimensional materials with both parallel and perpendicular multiple bond arrays using designed tetradentate ligands.[9-11] Here we report that $Mo_2(O_2CCH_3)_4$ reacts with the cluster acid $(CO)_9Co_3(\mu_3\text{-}CO_2H)$ to form three related high nuclearity clusters of clusters with the general formula $Mo_2\{\mu_2\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_m(CH_3CO_2)_{4-m}[(CO)_9Co_3(\mu_3\text{-}CCO_2H)]_n$ (m = 3, n = 0, I; m = 4, n = 0, II; m = 4, n = 2, III).

$Mo_2(CH_3CO_2)_4$ reacts with 2 equiv of $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ in THF at room temperature to give a deep midnight blue solution. On immediate cooling, a toluene extract gave needle-like blue-black crystals (73%) that were characterized as the solvated

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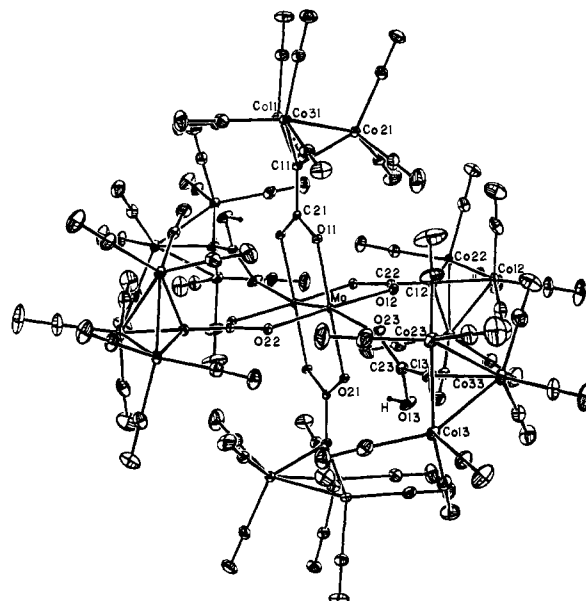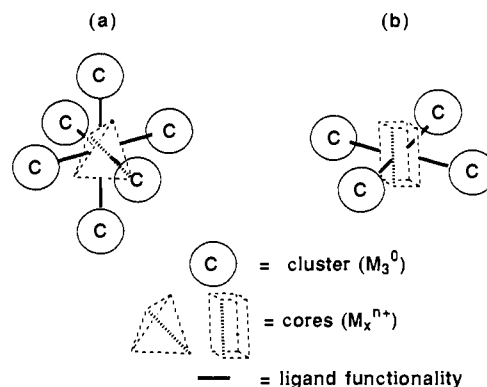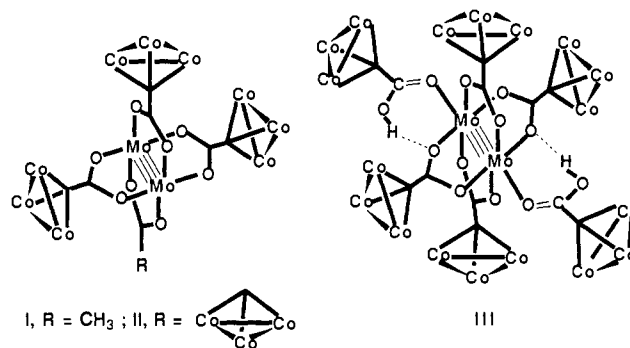

Figure 1. ORTEP plot (30% thermal ellipsoids) and selected bond distances (Å) and angles (deg) for III: Mo–Mo′ 2.1126 (3), Mo–O11 2.089 (1), Mo–O12 2.104 (1), Mo–O21 2.124 (1), Mo–O22 2.089 (1), (Co–Co)$_{eq,av}$ 2.47 (1), (Co–Co)$_{ax,av}$ 2.475 (3); (Mo–Mo–O)$_{eq,av}$ 92 (1), O11–C21–O21 120.7 (2), O12–C22–O22 122.2 (2).

Scheme I

Scheme II

I, R = CH₃ ; II, R = C⟨Co⟩Co III

tricluster-substituted species I·C₆H₅CH₃.[12] Crystallization at room temperature for days yielded both barlike crystals (~15%) and large pseudorhombohedral crystals (1–2 mm in size, ~40%). The latter crystals were selected and characterized as the tetracluster-substituted, cluster acid adduct III.[13] Another compound,

(12) Data for I: ¹H NMR (300 MHz, CD₂Cl₂) 2.34 (s, 3 H), 2.59 (s, 3 H), 7.20 (m, 5 H) arising from one acetae and a solvate toluene; FT-IR (KBr) CH₃ 2950 vw, (CO)₉Co₃C 2106 s, 2052 vs, 2048 vs, 2045 vs, COO⁻ 1518 w, 1494 w, 1448 m, 1440 m, 1366 m. Anal. Calcd for Mo₂Co₉C₄₂O₃₅H₁₁: Co, 29.50; Mo, 10.67; C, 28.06; H, 0.61. Found: Co, 29.20; Mo, 10.10; C. 27.94; H, <0.5.

II, was obtained (60%) by using 6 equiv of $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ along with a mixed solvent system of toluene and THF.[14] Compounds **I** and **III** produced X-ray quality crystals.[15,16]

Considering published information on the carboxylate exchange reaction,[10] the clean, quantitative reaction described above at room temperature is surprising. We know that there is substantial electronic interaction between the $(CO)_9Co_3C$ fragment and the $(COO)^-$ functional group,[2] and this, along with the substantial steric bulk of the cluster, presumably makes $[(CO)_9Co_3(\mu_3\text{-}CCO_2)]^-$ a much better ligand than acetate.

Structural representations of **I–III** (Scheme II) and an ORTEP plot of **III** (Figure 1) show that the three compounds differ only the nature of the axial ligation. For **III** the structural features in the vicinity of Mo_2^{4+} are similar to those in published structures.[6] In this case two cluster carboxylic acids occupy the axial positions of Mo_2^{4+} with a nonbonding Mo–O distance of 2.515 (2) Å and form hydrogen bonds between the axial cluster acid proton and an equatorial carboxylate oxygen O21. The hydrogen bonding elongates the Mo–O21 distance [2.124 (1) Å]. There are no significant structural differences among the six tricobalt clusters surrounding the Mo_2^{4+} core.

The symmetric A_1 stretching mode of the carbonyl ligands on the tricobalt cluster alkylidyne is a sensitive probe of the charge density on the Co_3 unit.[17] In $M^{II}_4[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$, M = Zn, Co^{I-3}, the cores behave essentially like a proton to the cluster carboxylates, and the A_1 mode has the same frequency, within experimental error, as in the uncoordinated acid. However, for the title compounds, the A_1 frequencies are at lower energy $(2103\text{–}2106\ cm^{-1})$ compared to those $(2111\ cm^{-1})$ in the uncoordinated cluster acid. This reveals an increase in the electron density on the equatorial tricobalt clusters of **I–III** compared to the free acid. Although the differences are small, they are real as **III**, which contains both four equatorial carboxylates and two axially coordinated cluster acids, exhibits both A_1 modes (2111 and 2105 cm^{-1}) in a 1:2 ratio.[14]

Although **I** and **III** are soluble in hydrocarbons and ethers, **II** has very poor solubility in the same solvents. This could result from a strong intermolecular axial interaction between the molybdenum of one molecule and a carboxylate oxygen of another, as has been well established in other systems.[6,10] Note that the electron donation from Mo_2^{4+} to the cobalt cluster makes Mo_2^{4+} more electrophilic, which in turn should enhance this interaction.

Another interesting feature of the title compounds is their intense midnight blue color (**I**, 572 nm, $\epsilon_{mole} = 22\,000\ cm^{-1}\ M^{-1}$; **III**, 536 nm, $\epsilon_{mole} = 31\,000\ cm^{-1}\ M^{-1}$) vs pale yellow color in starting material $Mo_2(O_2CCH_3)_4$ (435 nm, $\epsilon_{mole} = 100\ M^{-1}\ cm^{-1}$)[10,18] and purple-brown $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ (510 nm, $\epsilon_{mole} = 1300$; 370 nm, $\epsilon_{mole} = 3300$).[17,19,20] The ionization potentials

of $Mo_2(CH_3CO_2)_4$[21] and $(CO)_9Co_3(\mu_3\text{-}CCH_3)$[20] combined with HOMO–LUMO gaps derived from Fenske–Hall calculations[22] for the same molecules and, separately, direct calculations on $Mo_2(CH_3CO_2)_3[(CO)_9Co_3(\mu_3\text{-}CCO_2)]$ suggest that a $\delta(Mo_2^{4+})$ → $\sigma^*(Co_3)$ transition is responsible for the intense color. That is, in both approaches the ~4-eV gap between the δ and δ^* levels of the Mo_2^{4+} core contains a single empty orbital corresponding to the $\sigma^*(Co_3)$ orbital of the cobalt cluster. Because the extinction coefficient falls in the range of 10^4–$10^5\ cm^{-1}\ M^{-1}$, this absorption is allowed. The calculations suggest that it can be considered as a type of metal–ligand charge-transfer band but one where the final state now has high metal character due to the presence of the metal cluster substituent.

Supplementary Material Available: Tables of crystal structure analysis data which include atomic coordinates for all atoms and anisotropic thermal parameters for non-hydrogen atoms (14 pages); table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Conformational Studies of Sialyl Lewis X in Aqueous Solution

Ying-Chih Lin,[‡] Conrad W. Hummel, Dee-Hua Huang, Yoshitaka Ichikawa, K. C. Nicolaou,[†] and Chi-Huey Wong*

Department of Chemistry
The Scripps Research Institute, 10666 North Torrey
Pines Road, La Jolla, California 92037

The tetrasaccharide sialyl Lewis X (sialyl Le^x, Figure 1) NeuAcα(2→3)Galβ(1→4)[Fucα(1→3)]GlcNAc has recently been demonstrated to be the ligand of endothelial leukocyte adhesion molecule-1 (ELAM-1).[1] This discovery has led to the development of effective methods for the synthesis of sialyl Le^x and its derivatives as potential antiinflammatory agents. Both chemical[2,3] and enzymatic[4] methods are available for the synthesis of sialyl Le^x and its analogs. In order to further understand the structure–function relation of sialyl Le^x and to develop sialyl Le^x mimetics, we report our conformational study of sialyl Le^x based on two-dimensional NMR techniques in combination with MM2 molecular mechanics calculations.

It has been indicated in the early work of Lemieux[5] that polysaccharides are capable of adopting ordered conformations which place sugar unit and functional groups at regular and predictable

(13) Data for **III**: FT-IR (KBr) $(CO)_9Co_3^-$ 2111 m(sh), 2105 s, 2042 vs (br), COOH 1646 s, COO^- 1449 m, 1362 m.

(14) Data for **II**: FT-IR (KBr) $(CO)_9Co_3^-$ 2104 s, 2075 s(sh), 2042 vs, 2022 s, 2013 s, COO^- 1453 m, 1375 m(br). Anal. Calcd for $Mo_2Co_{12}C_{44}O_{44}$: Co, 33.18; Mo, 9.00; C, 24.79. Found: Co, 33.34; Mo, 8.31; C, 23.03.

(15) Crystal data for $Mo_2Co_9C_{42}O_{35}H_{11}$ (**I**): space group *Pmma*; $a = 42.738$ (16), $b = 15.110$ (3), $c = 8.988$ (3) Å; $V = 5804$ Å^3, d(calcd) = 2.06 g/cm^3, d(obsd) = 2.04 g/cm^3; $M_r = 1797.8$; $Z = 4$, $\mu = 19.3\ cm^{-1}$. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromated Mo Kα X-radiation source. Although the structure remains unsolved because of a space group ambiguity, the cell and density data confirm the formula.

(16) Crystal data for $Mo_2Co_{18}C_{66}O_{66}H_2$ (**III**): space group triclinic $P\bar{1}$; $a = 12.976$ (2), $b = 14.347$ (5), $c = 15.584$ (5) Å; $\alpha = 89.38$ (2), $\beta = 66.07$ (2), $\gamma = 68.90$ (1)°; $V = 2442.7$ Å^3, d(calcd) = 2.11 g/cm^3, d(obsd) = 2.20 g/cm^3; $M_r = 3103.4$; $Z = 1$, $\mu = 33.1\ cm^{-1}$. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromated Mo Kα X-radiation source. Crystallographic computations were carried out on a VAXstation 3200 computer using the SDP/VAX software. The structure was solved by a combination of direct methods and difference Fourier syntheses. Full-matrix least-squares refinements were employed. $R(R_w) = 0.043(0.053)$ (685 variables refined including the hydrogen atom parameters) for 11 825 reflections $[F_o > 3.0\sigma(F_o)]$ of 13 329 independent reflections collected over the 2θ range $3.0° \leq 2\theta \leq 58.7°$.

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