When concentrations of 6-dodecyl-2-naphthol considerably in excess of monolayer coverage were spread on the surface, visible aggregates were seen to form. The much more intense emission spectrum of these aggregates is shown in Figure 2 and is quite different from that of the monolayer. The fluorescence excitation spectrum of these aggregates, monitoring emission at 375 nm, is very similar to that of 6-dodecyl-2-naphthol in hexane and 2-naphthol in ethanol, showing that the excited state interaction is responsible for the red-shifted emission.

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Cluster Complexes of Tridentate Sulfate and (Hydrogen) Phosphate. The Crystal Structure of $H_2Os_3(CO)_9(\mu_3\text{-}O_3SO)$

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The coordination chemistry of tetrahedral oxyanions such as SO_4^{2-} and PO_4^{3-} has been well studied,[1] and examples of these anions functioning as unidentate, bidentate, and bridging ligands are numerous.[2] The most common oxyanion bridge connects two oxygen atoms to different metal atoms, but in some cases dimeric chelating arrangements are found in which four oxygen atoms are evenly divided between two metal atoms.[3] In addition polymeric structures containing bridging tridentate oxyanions have been confirmed.[4] We have now synthesized and structurally characterized $H_2Os_3(CO)_9(\mu_3\text{-}O_3SO)$, which we believe contains the first example of a tridentate sulfate ligand in a nonpolymeric complex.[5] This robust product is of particular interest because sulfate ligands are usually found in complexes containing metals in medium to high oxidation states and because organometallic sulfate complexes are uncommon.[6] By an alternative route we have obtained and characterized the analogous $H_2Os_3(CO)_3(\mu_3\text{-}O_3POH)$.

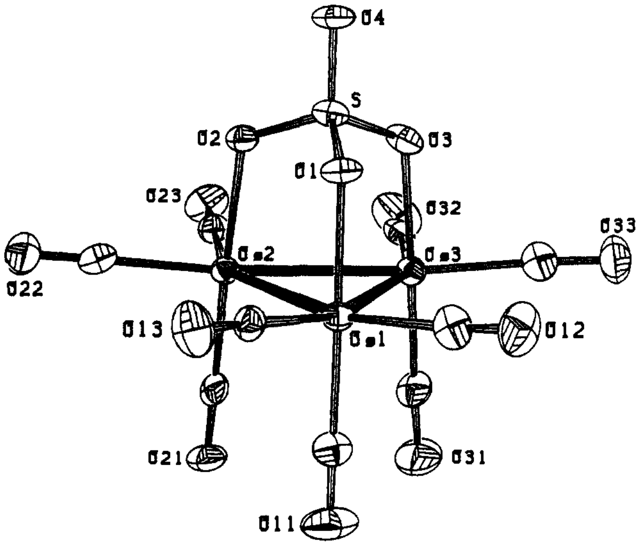

Figure 1. ORTEP diagram of $H_2Os_3(CO)_9(\mu_3\text{-}O_3SO)$. Metal-metal distances are Os(1)–Os(2) = 3.029 (1), Os(1)–Os(3) = 3.050 (1), and Os(2)–Os(3) = 2.820 (1) Å. The hydrogen atoms, which were not located, are assumed to bridge the Os(1)–Os(2) and Os(1)–Os(3) edges. Other important distances are Os(1)–O(1) = 2.11 (1), Os(2)–O(2) = 2.14 (1), Os(3)–O(3) = 2.13 (1), S–O(1) = 1.51 (1), S–O(2) = 1.49 (1), S–O(3) = 1.51 (1), and S–O(4) = 1.42 (1) Å.

Treatment of solid $H_3Os_3(CO)_9(\mu_3\text{-}CH)$[7] with 98% sulfuric acid causes the evolution of gas and formation of a light yellow solution. Dilution of the solution with water leads to a pale yellow precipitate, which can be separated, washed with water, and vacuum-dried. Pale yellow prisms of the product (67%) are obtained from dichloromethane–methanol, and its formulation as $H_2Os_3(CO)_9(SO_4)$ is established by elemental analysis and spectroscopic methods.[8]

The molecular structure of $H_2Os_3(CO)_9(\mu_3\text{-}O_3SO)$ is shown in Figure 1.[9] The isosceles triangle of osmium atoms is capped by a tridentate, triply bridging sulfate ligand. There are modest structural changes in the sulfate moiety relative to the free, tetrahedral ion (d(S–O) = 1.49 Å[10]). The interior O_c–S–O_c angles average 107.9°, whereas the exterior O_c–S–O_t angles average 111.0°. Also, the S–O_c distances are longer (1.50 (2) Å av) than the S–O_t distance (1.42 (1) Å).[11] This coordination mode is well reflected in the IR spectrum; viz., a strong band at 1275 cm^{-1} is due primarily to stretching the S–O_t bond, whereas three (C_s symmetry) weaker bands at 1047, 1020, and 956 cm^{-1} are due to the S–O_c bonds.[12] The fit of the capping sulfate ligand to the metal triangle is reasonably good; the Os–O_c bonds are tilted slightly inward (mean Os–Os–O_c angle = 82.7°), whereas the corresponding trans carbonyls are splayed slightly outward (mean Os–Os–C angle = 95.3°). This contrasts with the case of $Ru_3(CO)_9(\mu_3\text{-}MeSi(n\text{-}Bu_2P)_3)$,[13] in which the tripod ligand "bite" is slightly larger than the metal triangle, leading to obtuse Ru–Ru–P angles.[14]

Clusters of formulation $H_2Os_3(CO)_9(X)$ (X = S, C_6H_4, CCH_2), in which X is a four-electron donor, have been prepared previously by the direct reaction of $Os_3(CO)_{12}$ with H_2X.[15] The reaction

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(9) The complex crystallizes in monoclinic space group $C2/c$ with a = 30.11 (1) Å, b = 8.492 (3) Å, c = 13.864 (4) Å, β = 100.39 (3)°, and V = 3487 (2) Å. The calculated density is 3.508 g cm^{-3} for Z = 8 and mol wt 920.77. Diffraction data were collected (Mo Kα) and numerically corrected for absorption. The structure was solved by direct methods and refined by least-squares difference Fourier methods to R = 4.4% and R_w = 5.3%.

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of H_2SO_4 with $Os_3(CO)_{12}$, however, gives the cationic species $HOs_3(CO)_{12}^+$ and $HOs(CO)_5^+$.[16] Protonation of $H_3Os_3(CO)_9(\mu_3\text{-CH})$ with H_2SO_4 presumably occurs on the Os-C bond;[17,18] the evolved gas is predominantly methane.[19] MO calculations on the analogous $H_3Ru_3(CO)_9(\mu_3\text{-CY})$ clusters show that the HOMO is mainly Ru-C in character.[22]

Phosphoric acid does not react with $H_3Os_3(CO)_9(\mu_3\text{-CH})$ under mild conditions. However, addition of trifluoromethanesulfonic acid leads to gas evolution and a yellow solution. The species present in solution have not yet been characterized but presumably involve complexes of the $CF_3SO_3^-$ ion.[23] Addition of P_4O_{10}-saturated phosphoric acid to this solution, followed by dilution with water, produces a light yellow precipitate. Analytical and mass spectral data are consistent with the expected phosphate complex,[24] but the IR spectrum clearly shows that it is best formulated as a hydrogen phosphate species, i.e., $H_2Os_3(CO)_9(\mu_3\text{-}O_3POH)$. In particular, a strong, H-bonded OH stretch occurs at 3400 cm^{-1} and a band appropriate for a P=O stretch is absent.[25] A similar bonding mode has been observed for layered metal phosphates, e.g., $\alpha\text{-Zr}(HPO_4)_2\cdot H_2O$[26] and $(VO)_2H_4P_2O_9$.[27]

These oxyanion complexes are of interest not only as unique molecular examples of the tridentate, triply bridging coordination mode but also as models for the interaction between metal clusters and oxide supports. In particular, they are a suggestive representation for the "decoration" of metal particles by MO_x moieties, which has been proposed to be involved in the strong metal-support interaction (SMSI).[28] Furthermore, they may be related to the oxyanion species identified as adsorbed on platinum electrodes.[29] The structural and reactivity implications of these "hard-soft" complexes are being pursued.

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Supplementary Material Available: Tables of final positional parameters and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(18) Keister has shown that protonation of $H_3Ru_3(CO)_9(\mu_3\text{-}CCH_3)$ occurs at an Ru-C bond: Bower, D. K.; Keister, J. B., unpublished results.

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On the Origins of Stereoselectivity in "Chelation Controlled" Nucleophilic Additions to β-Alkoxy Aldehydes: Solution Structures of Lewis Acid Complexes via NMR Spectroscopy

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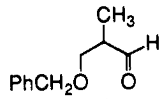
The area of "acyclic stereochemical control" has assumed a position of prominence in organic synthetic methodology in recent years. Many bond-forming processes utilized in this context have exploited "anti-Cram" or "chelation-controlled" phenomena[1] to obtain high levels of diastereofacial selectivity in nucleophilic additions to carbonyl compounds. Despite the amazing number of impressive examples that exploit such a phenomenon, i.e., presumed conformational biasing of substrate prior to reaction, no general study of the structures of such intermediates has been reported to date.[2] Our own interests in the mechanistic details and stereochemical course of additions of certain "storable organometallics"[3,4] to carbonyl compounds has prompted us to initiate a long-range program directed toward obtaining a fundamental understanding of this process, part of which requires a knowledge of the structures of putative complexed intermediates derived from alkoxy carbonyl compounds *in solution*. The results of some of our initial investigations are sufficiently compelling and relevant to the progress of much current research that we report them in this format.

Of crucial importance to this first report is the realization that, with β-alkoxy aldehydes **1** and **2**, attack of certain allylsilanes or stannanes (in the presence of bidentate Lewis acids) apparently occurs preferentially from the face opposite the methyl groups.[5] There is no obvious explanation for this result, particularly since all literature interpretations position the C_2 or C_3 substituents in pseudoequatorial positions in the presumed intermediate complex.[6] We record herein the resolution of this issue and the first direct experimental evidence regarding the origins of diastereofacial selectivity in such systems, via variable-temperature NMR spectroscopy of the complexes formed with aldehydes **1** and **2** with $TiCl_4$, $SnCl_4$, and $MgBr_2\text{-}OEt_2$ (Figure 1).



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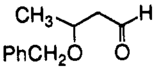

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We begin with the results for **1** with $TiCl_4$. ^1H and ^{13}C NMR spectra[7] were recorded at various temperatures (−80, −60, −40,

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