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Figure 2. Molecular orbital diagram showing the interaction of the π_2 and $\pi_3{}^*$ orbitals of *cis*- and *trans*-butadiene with the frontier orbitals of the CpMo(NO) fragment. The Mulliken populations of the diene orbitals after complexation are given below the sketch of each (free ligand populations: $\pi_2 = 2.0$; $\pi_3{}^* = 0.0$). The paired electrons indicate the HOMO of each species.

reaction 1 is established by the fact that it isomerizes irreversibly to **2** (with some attendant decomposition) in these solutions. This isomerization is rapid at 20 °C in donor solvents such as THF ($t_{1/2} \sim 5$ min) but slower in nondonor solvents such as benzene ($t_{1/2} \sim 1$ day). Once formed, the bound *trans*-diene in **2** (or in any other known CpMo(NO)(η^4-*trans*-diene) complex)[3] does not revert to its cis form even upon heating to the decomposition point of the complex in various solvents.

To rationalize the unprecedented stability of **2** over **1** in terms of their electronic structures, we have performed Fenske–Hall MO calculations[11] on the model systems containing *cis*- and *trans*-butadiene bound to CpMo(NO) in the fashion found in **1** and CpMo(NO)(η^4-*trans*-2,5-dimethyl-2,4-hexadiene),[3] respectively.[12] These calculations lead to the orbital interaction diagrams and Mulliken populations presented in Figure 2. In both model complexes there is substantial donation from the diene π_2 orbital to the metal and back-donation from the metal to the diene $\pi_3{}^*$ orbital. The *cis*-diene is calculated to be both a weaker donor and stronger acceptor than the *trans*-diene; in spite of this, the NO 2π population is greater in the cis complex (1.57 e) than in the trans complex (1.51 e), in accord with the IR data for **1** and **2**. The greater stability of the trans complex, as evidenced by a HOMO energy ca. 0.9 eV lower than that of the cis complex, results from the asymmetry of the *trans*-diene ligand which is better able to stabilize the high-lying occupied orbitals of the CpMo(NO) fragment.

Finally, the results of these calculations (taken in conjunction with those performed on the related $Cp_2Zr(\eta^4$-butadiene) complexes)[4] suggest the following electronic criteria which a monometallic fragment (L_nM) must satisfy in order to coordinate butadienes preferentially in a trans manner: (1) L_nM must possess valence orbitals such that its HOMO and LUMO are coplanar and have σ and π rotational symmetry, respectively, with respect to the centroid of the diene ligand, and (2) L_nM must be relatively electron deficient to minimize electron donation from its HOMO and to maximize acceptance of electron density into its LUMO and higher lying unoccupied molecular orbitals. Experiments are currently in progress to test the general applicability of these criteria.

(11) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.
(12) Fenske–Hall calculations were carried out as described in ref 13.
(13) Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554.

Fluorescence of 6-Dodecyl-2-naphthol in Monolayers at the Air–Water Interface

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A number of different sorts of measurements have demonstrated that the apparent dielectric constant of the interfacial region of micelles, bilayers, and microemulsions is substantially lower than that of bulk water.[1–10] Although it has not always been recognized,[11] one result of this will be a pK_a shift for acid groups located at the interfaces of uncharged micelles.[1,2] By comparing the observed shifts with those obtained in suitable mixed solvents of known dielectric constant, an estimate of interfacial dielectric constant can be made.[1] Measurements with probe molecules whose absorption (solvatochromic probes)[4–6] or fluorescence spectrum[3,7,8] is sensitive to polarity provide independent confirmation of an interfacial dielectric constant ranging from 15 to 55 for various systems. Kinetic measurements on the hydrated electron in microemulsions are also in accord with these estimates.[9] The shift in pK_a of acid groups due to nonelectrostatic effects is also seen in cast monolayer films on solid substrates[2,12,13] but has not to date been demonstrated in air–water monolayers. It is not clear whether this reduced dielectric constant is entirely explicable in terms of the reduced concentration of water in an interface consisting of water and head groups[14] or whether there is an additional contribution due to water structuring associated with the proximity of the hydrocarbon tail groups.[14,6] Recent work on excited-state proton dissociation[15,16] has emphasized the importance of the molecular structure and dynamics of water and suggests that the dielectric constant may not be the most ap-

(1) Fernandez, M. S.; Fromherz, P. *J. Phys. Chem.* **1977**, *81*, 1755.
(2) Lovelock, B.; Grieser, F.; Healy, T. W. *J. Phys. Chem.* **1985**, *89*, 501.
(3) Law, K. Y. *Photochem. Photobiol.* **1981**, *33*, 799.
(4) Zachariasse, K. A.; Van Phuc, N.; Kozankiewicz, B. *J. Phys. Chem.* **1981**, *85*, 2676.
(5) Mukerjee, P.; Cardinal, J. R. *J. Phys. Chem.* **1978**, *82*, 1620.
(6) Ramachandran, C.; Pyter, R. A.; Mukerjee, P. *J. Phys. Chem.* **1982**, *86*, 3198.
(7) Kalyanasundaram, K.; Thomas, J. K. *J. Phys. Chem.* **1977**, *81*, 2176.
(8) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188.
(9) Thomas, J. K.; Grieser, F.; Wong, M. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 937.
(10) Mukerjee, P.; Ray, A. *J. Phys. Chem.* **1966**, *70*, 2144.
(11) Goddard, E. D.; Ackilli, J. A. *J. Colloid Sci.* **1963**, *18*, 585.
(12) Fromherz, P. *Biochim. Biophys. Acta* **1973**, *323*, 326.
(13) Lovelock, B.; Grieser, F.; Healy, T. W., submitted for publication in *Langmuir*.
(14) Mukerjee, P.; Cardinal, J. R.; Desai, N. R. In *Micellization, Solubilization and Microemulsions*; Mittal, K. L., Ed.; Plenum Press: New York, 1977; Vol. 1, p 241.
(15) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920.
(16) Webb, S. P.; Philips, L. A.; Clark, J. H.; Lee, J.; Robinson, G. W. *J. Phys. Chem.*, in press.

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propriate parameter for the discussion of proton transfer at aqueous/monolayer interfaces. To be weighed against this are the data from the "polarity" probes, which should not be influenced by the kinetic considerations of ref 15 and 16 but which nevertheless point to reduced polarity in the interfacial region. Whatever the case, the use of the term "apparent interfacial dielectric constant" is widespread in the surface chemical literature and will be continued here.

We have been interested in the possibility of using suitable long-chain aromatic hydroxy compounds in kinetic fluorescence studies of proton dissociation at interfaces. Molecules such as 2-naphthol, when excited in neutral aqueous solution, undergo spontaneous deprotonation as a result of the pK_a in the excited state being some 6 or 7 units lower than that of the ground state.[15-19] As the rate of proton dissociation is markedly dependent on the solvent structure,[15,16,20,21] studies of the rate of dissociation should provide insights into the nature of the solvent in the vicinity of the interface.

As a first step in this direction we have synthesized 6-dodecyl-2-naphthol and carried out some steady-state fluorescence measurements on monolayers of this molecule at the air–water interface. These studies reveal that, unlike neutral aqueous 2-naphthol, 6-dodecyl-2-naphthol in the monolayer over neutral water, and in micelles, undergoes no excited-state dissociation. One way of describing this inhibition of proton dissociation is to attribute to the interfacial environment a dielectric constant lower than that of pure water.

All measurements were carried out in a 27 × 17 × 1.5 cm Teflon Langmuir trough with a motor-driven Teflon barrier. Surface pressure measurements were made by the Wilhelmy plate method, using a 4-cm-wide mica plate suspended from a calibrated Shinkoh, 2-g weight capacity strain gauge feeding a chart recorder. The boom was swept at a rate of 3 cm min^{-1}. The trough and barrier were cleaned with hexane, the mica plate was rinsed in nitric acid, and impurities were swept off the water surface before the monolayer was spread. Milli-Q filtered water (κ < 10^{-6} S m^{-1}, γ_0(25 °C) = 72 mN m^{-1}) was used as the subphase. The efficacy of these procedures was checked by recording the surface pressure–area isotherm for stearic acid. Good agreement with the literature value for the limiting surface area per molecule was obtained. For the 6-dodecyl-2-naphthol monolayers a 1.66 mM solution in hexane was used and 0.1 mL, corresponding to ca. 10^{17} molecules, was spread on the surface.

Fluorescence measurements were made on a Perkin-Elmer LS-5 spectrofluorimeter. The instrument was fitted with a bifurcated fiber optic system, one bundle of fibers conveying exciting light to the surface, the other conveying fluorescence to the emission monochromator. The two bundles terminated in a single monitoring head positioned ca. 2 mm above the surface. Although the pulsed excitation, gated detection mode of operation of the fluorimeter should eliminate stray light, some 50-Hz interference was encountered and to eliminate this the trough was screened from room light. With a clean water surface only, some "background" is still detected, due probably to the fibers themselves, following leakage of exciting light into the "emission" fibers. The fluorimeter has the capacity to sum multiple scans as well as to subtract spectra. The usual procedure was thus to make 30 scans of the spectrum and the background and then subtract the latter.

The surface pressure–area isotherm for 6-dodecyl-2-naphthol exhibited "gaseous", "expanded liquid", and "condensed liquid" regions, with no evidence of any inflections. Extrapolation of the steep, high-pressure region curve to zero surface pressure yielded a value of 32 ± 2 Å^2 per molecule. This value is similar to that
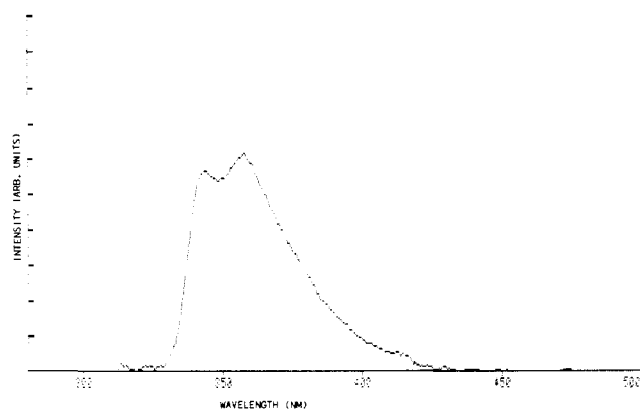

Figure 1. Fluorescence spectrum of a 6-dodecyl-2-naphthol monolayer at the air–water interface.
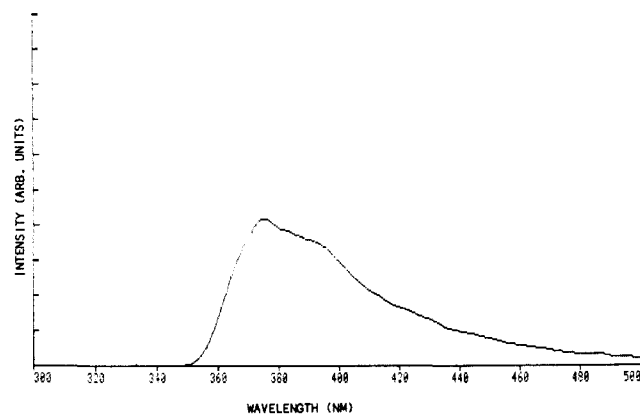

Figure 2. Fluorescence emission of surface aggregates of 6-dodecyl-2-naphthol.

found earlier for 4-octadecyloxy-1-naphthoic acid.[22] Monolayer collapse occurred at a surface pressure of ca. 34 mN m^{-1}. The fluorescence spectrum of the monolayer, compressed somewhat beyond collapse point and recorded with excitation and emission bandwidths of 15 and 5 nm, respectively, and an excitation wavelength of 290 nm, is shown in Figure 1. The spectrum consists of a single band showing two maxima at ca. 343 and 357 nm. This is very similar to the emission of 6-dodecyl-2-naphthol in hexane. In particular there is no evidence of a second band attributable to the anion[18] in the region of 420 nm. The same spectrum, although less intense, is obtained for less compressed monolayers. The absence of "anion" emission shows that, unlike neutral aqueous 2-naphthol, 6-dodecyl-2-naphthol in the monolayer does not undergo appreciable excited-state dissociation. In a recent study of the excited-state dissociation of 2-naphthol in water–methanol mixtures, it was found that dissociation becomes negligible above a volume fraction of methanol of ca. 0.5.[15] It was shown that proton transfer to water depends on the formation of a suitable four-water cluster. Thus it can be inferred that in the water adjacent to the monolayer these clusters are not readily formed. A methanol volume fraction of 0.5 corresponds to a dielectric constant of 60.[23] On this basis we can place an upper limit of 60 on the apparent dielectric constant experienced by the 2-naphthol head group in the monolayer situation. The observation of splitting in the 350-nm emission band also supports this conclusion. While no splitting is seen for aqueous 2-naphthol,[18,24] the emission spectrum of the monolayer is rather similar to that of 2-naphthol in ethanol,[25] supporting the idea that the 2-naphthol head group experiences an appreciably nonaqueous environment.

(17) Martynov, I. Y.; Demyashkevich, A. B.; Uzhinov, B. M.; Kuzmin, M. G. Russ. Chem. Rev. (Engl. Transl.) 1977, 46, 1.

(18) Ofran, M.; Feitelson, J. Chem. Phys. Lett. 1973, 19, 427.

(19) Smith, K. K.; Kaufmann, K. J.; Huppert, D.; Gutman, M. Chem. Phys. Lett. 1979, 64, 522.

(20) Huppert, D.; Kolodney, E. Chem. Phys. 1981, 63, 401.

(21) Huppert, D.; Kolodney, E.; Gutman, M.; Nachliel, E. J. Am. Chem. Soc. 1982, 104, 6949.

(22) Hayes, D., private communication.

(23) Timmermans, J. The Physico-chemical Constants of Binary Systems in Concentrated Solutions; Interscience Publishers: New York, 1960; Vol. 4, p 168.

(24) Harris, C. M.; Selinger, B. K. J. Phys. Chem. 1980, 84, 891.

(25) Berlman, I. B. Handbook of Fluorescence Spectra of Aromatic Molecules, 2nd ed.; Academic Press: New York, 1971; p 340.

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.

Cluster Complexes of Tridentate Sulfate and (Hydrogen) Phosphate. The Crystal Structure of H2Os3(CO)9(μ3-O3SO)

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The coordination chemistry of tetrahedral oxyanions such as SO4²⁻ and PO4³⁻ 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 H2Os3(CO)9(μ3-O3SO), 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 H2Os3(CO)3-(μ3-O3POH).

Treatment of solid H3Os3(CO)9(μ3-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 H2Os3-
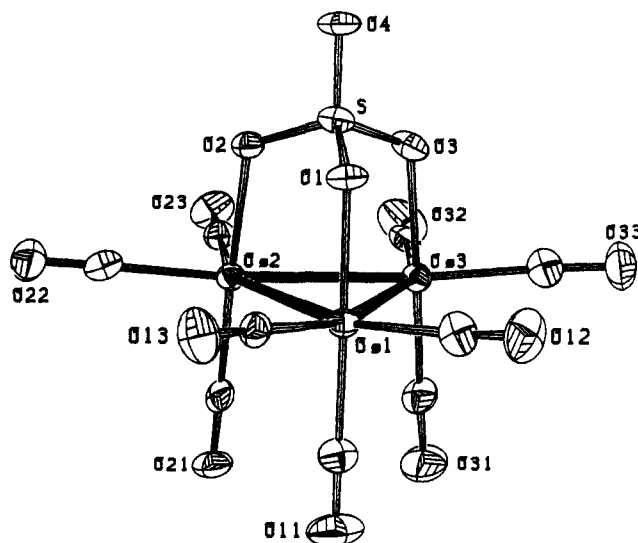

Figure 1. ORTEP diagram of H2Os3(CO)9(μ3-O3SO). Metal-metal distances are Os(1)-Os(2) = 3.029 (1), Os(1)-Os(3) = 3.050 (1), and Os(2)-Os(3) = 2.820 (1) Å. The hydrogen atoms, which were not located, are assumed to bridge the Os(1)-Os(2) and Os(1)-Os(3) edges. Other important distances are Os(1)-O(1) = 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.

(CO)9(SO4) is established by elemental analysis and spectroscopic methods.[8]

The molecular structure of H2Os3(CO)9(μ3-O3SO) 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 Oc-S-Oc angles average 107.9°, whereas the exterior Oc-S-Ot angles average 111.0°. Also, the S-Oc distances are longer (1.50 (2) Å av) than the S-Ot 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-Ot bond, whereas three (Cs symmetry) weaker bands at 1047, 1020, and 956 cm⁻¹ are due to the S-Oc bonds.[12] The fit of the capping sulfate ligand to the metal triangle is reasonably good; the Os-Oc bonds are tilted slightly inward (mean Os-Os-Oc 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 Ru3-(CO)9(μ3-MeSi(n-Bu2P)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 H2Os3(CO)9(X) (X = S, C6H4, CCH2), in which X is a four-electron donor, have been prepared previously by the direct reaction of Os3(CO)12 with H2X.[15] The reaction

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; pp 175, 474.

(2) (a) Sisley, M. J.; Swaddle, T. W. *Inorg. Chem.* **1981,** *20,* 2799. (b) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982,** *21,* 2889. (c) Bhaduri, S.; Johnson, B. F. G.; Khair, A.; Ghatak, I.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1980,** 1572. (d) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975,** *14,* 405. (e) Green, M.; Taylor, R. S.; Sykes, A. G. *J. Inorg. Nucl. Chem.* **1971,** *33,* 2157.

(3) (a) Phillippi, M. A.; Baenziger, N.; Goff, H. M. *Inorg. Chem.* **1981,** *20,* 3904. (b) Lindner, E.; Kunze, U.; Ritter, G.; Haag, A. *J. Organomet. Chem.* **1970,** *24,* 119.

(4) Toironem, J.; Lauri, N. *Inorg. Chem.* **1983,** *22,* 1557.

(5) An arsenato cluster, Re3Br3(Me2SO)3(AsO4)2, has been reported and a structure with two tridentate μ3-O3As=O ligands was suggested on the basis of IR analysis; a phosphato complex was also reported but not described: Cotton, F. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1966,** *88,* 1882.

(6) (a) Green, M. L. H.; Lynch, A. H.; Swanwick, M. G. *J. Chem. Soc., Dalton Trans.* **1972,** 1445. (b) Ryan, R. R.; Kubas, G. J. *Inorg. Chem.* **1978,** *17,* 637.

(7) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977,** *99,* 5225.

(8) Anal. (C9H2O13SOs3) C, H, Os. Mass spectrum (¹⁹²Os, ³²S), *m/z* 926 (M⁺) plus fragment ions. ¹H NMR (acetone-*d6*) δ -12.04 (s). IR (CH2Cl2) ν(CO) 2140 (m), 2108 (s), 2081 (vs), 2048 (s), 2038 (m), 2010 (m) cm⁻¹.

(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 (MoKα) 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 *Rw* = 5.3%.

(10) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1975; pp 584-587.

(11) Comparable differences between S-O(coord) and S-O(term) distances have been determined for binuclear bidentate sulfate ligands. See: Bancroft, C. P.; Cotton, F. A.; Falvello, L. R.; Han, S.; Schwotzer, W. *Inorg. Chim. Acta* **1984,** *87,* 147 and references therein.

(12) (a) Nakamoto, K.; Fujita, J.; Tamaka, S.; Kobayaski, M. *J. Am. Chem. Soc.* **1957,** *79,* 4904. (b) Lambert, J. B.; Shurvell, H. F.; Verbit, L; Cooks, R. G.; Stout, G. H. *Organic Structural Analysis*; Macmillan: New York, 1976; Chapter 5.

(13) DeBoer, J. J.; VanDoorn, J. A.; Masters, C. *J. Chem. Soc., Chem. Commun.* **1978,** 1005.

(14) For related work on a tripod ligand capping a triangular face of a tetrametallic cluster, see: Bahsoun, A. A.; Osborn, J. A.; Voelker, C.; Bonnet, J. J.; Lavigne, G. *Organometallics* **1982,** *1,* 1114.