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Supplementary Material Available: Structure factor table for DL-2-(α-hydroxybenzyl)oxythiamin chloride hydrochloride trihydrate, anisotropic thermal parameters, and table of interring separations (6 pages). Ordering information is given on any current masthead page.

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Communications to the Editor

Synthesis and Characterization of Bis(fulvalene)divanadium and the Crystal Structure of Its Oxidation Product, Bis(fulvalene)bis(acetonitrile)divanadium(III)-(*V–V*) Bis(hexafluorophosphate)-Acetonitrile (1/1)

Sir:

Because of the current interest in the structure and reactivity of coordinatively unsaturated metallocenes[1] and the formally analogous metallofulvalene derivatives,[2] we wish to report our initial synthetic, physical, and X-ray structural studies of the bis(fulvalene)divanadium system.

The neutral $(C_{10}H_8)_2V_2$ (**1**) was obtained by the reaction of $VCl_2 \cdot 2THF$[3] with 1 equiv of fulvalene dianion[2d] in refluxing THF. The dark purple air-sensitive product was isolated and purified by repeated sublimation under high vacuum at 230 °C.[4] The solubility of **1** in polar and nonpolar solvents is very low. The mass spectrum[5] and infrared spectrum of **1** are similar to those for the neutral bis(fulvalene)dimetal derivatives of Ni,[6a] Co,[6b] Fe,[6c] and Cr.[6b] Magnetic susceptibility measurements on solid samples indicate that **1** is diamagnetic from 4.2 to 100 K. This is consistent with the observed diamagnetism of both the dicationic and neutral derivatives of all bis(fulvalene)dimetal complexes studied to date, from vanadium, with 28[6b] and 30 valence electrons, respectively, to nickel, with 38 and 40[6a] valence electrons. The complete magnetic coupling found in **1**, compared to the "parent" vanadocene with an open-shell 15-electron structure and three unpaired electrons, can be rationalized by either a direct metal–metal interaction (bond) or by ligand-propagated exchange. Although X-ray crystallographic data for neutral $(C_{10}H_8)_2Ni_2$ clearly indicate the presence of a ligand-propagated exchange,[7] an assessment of the relative contributions from each exchange mechanism for electron-deficient early transition metal derivatives must await similar detailed structural information.

The oxidation of **1** with either 1 or 2 equiv of ferrocenium hexafluorophosphate per dinuclear vanadium complex in dry oxygen-free acetonitrile yields only a two-electron product, $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)_2(CH_3CN)_2V_2(III)(V\text{-}V)^{2+}][PF_6^-]_2 \cdot CH_3CN$ (**2**), that was isolated as brown microcrystals by the slow addition of toluene.[8] Magnetic susceptibility measurements in acetonitrile at 310 K by the Evans NMR method[9] indicate that **2** is paramagnetic with μ_{eff} = 2.9 BM per dinuclear vanadium complex. Measurements on solid samples from 4 to 80 K indicate a μ_{eff} = 3.0 BM. These results establish the presence of two unpaired electrons for the dinuclear metal complex. The infrared spectrum of **2** exhibits terminal nitrile stretches at 2320 and 2290 cm^{-1}.

Hygroscopic and air-sensitive single crystals of the acetonitrile solvate **2**, obtained by recrystallization from acetonitrile/benzene, are orthorhombic and noncentrosymmetric, space group $Cmc2_1$ ($C_{2v}{}^{12}$, No. 36), with a = 7.771 (1) Å, b = 20.556 (3) Å, c = 18.324 (3) Å, and Z = 4 ($[(C_{10}H_8)_2V_2(NCCH_3)_2][PF_6]_2 \cdot CH_3CN$ formula units). The various statistical indicators calculated with normalized structure factors, as well as all stages of the structure solution and refinement, were in agreement with the choice of a noncentrosymmetric space group. Diffracted intensities were measured for 2193 independent reflections having $2\theta_{\text{Mo}K\bar{\alpha}} < 58.7°$ on a computer-controlled Syntex P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (1° wide) ω scans. The structural parameters[10] have been refined to convergence [R = 0.045 for 949 independent reflections having $2\theta_{\text{Mo}K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$] in cycles of unit-weighted, full-matrix, least-squares refinement which employed anisotropic thermal parameters for all nonhydrogen atoms.

The structural analysis reveals that the crystal is composed of bis(fulvalene)bis(acetonitrile)divanadium(III)(*V–V*) dications (Figure 1), hexafluorophosphate anions, and acetonitrile molecules of crystallization. Although each $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)_2(CH_3CN)_2V_2]^{2+}$ unit is required to possess only crystallographic C_s-m symmetry (with the two vanadium atoms and the nonhydrogen atoms of their coordinated acetonitrile ligands lying in the mirror plane), the dication as a whole approximates rather closely idealized C_{2v} site symmetry with the pseudo-C_2 axis passing through the midpoints of the C_9–C_{10}' and V_a–V_b vectors of Figure 1. Bond lengths and angles for chemically equivalent groupings, averaged in accord with approximate C_{2v} molecular symmetry, include: V_a–V_b, 3.329 (4) Å; V–N, 2.09 (1,2,2,2) Å;[11] V–C, 2.28 (1,2,3,10)

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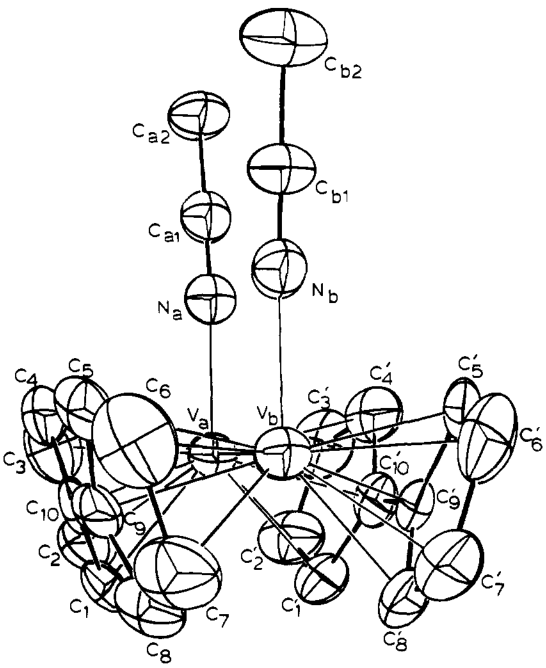

Figure 1. Perspective ORTEP drawing of the nonhydrogen atoms for the bis(fulvalene)bis(acetonitrile)divanadium(III) dication viewed approximately 10° off the crystallographic mirror plane which contains V_a, V_b, and their coordinated acetonitrile ligands. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Atoms V_a, N_a, C_{a1}, C_{a2}, and fulvalene atoms C_1–C_4 and C_{10} are related to the corresponding V_b, N_b, C_{b1}, C_{b2}, and fulvalene atoms C_5–C_8 and C_9, by a pseudo-mirror plane. Atoms labeled with a prime (′) are related to those without a prime by the crystallographic mirror plane.

Å;[11] C–C (intra-ring), 1,44 (2,2,5,10) Å; C_9–C_{10}, 1.45 (2) Å; N_a–C_{a1}, 1.13 (2,2,2,2) Å; C_{a1}–C_{a2}, 1.45 (3,1,1,2) Å; V–V–N, 89.1 (4,9,9,2)°;[11] V–N_a–C_{a1}, 171 (1,2,2,2)°;[11] N_a–C_{a1}–C_{a2}, 178 (2,1,1,2)°; C–C–C(intra-ring), 108 (1,1,3,10)°; and C–C_9–C_{10}, 125 (1,1,2,4)°.

Although each set of five carbon atoms which comprise the two rings of a fulvalene ligand are individually coplanar to within 0.007 Å, the entire ligand is folded with the mean planes for the two planar five-membered rings intersecting in a dihedral angle of 13.6°. The nature of this folding is such that the average $C_1 \cdots C_1'$, $C_2 \cdots C_2'$, $C_7 \cdots C_7'$, and $C_8 \cdots C_8'$ separation for both halves of the dication is 2.98 (3,3,4,4) Å, while the average $C_3 \cdots C_3'$, $C_{10} \cdots C_{10}'$, $C_6 \cdots C_6'$, and $C_9 \cdots C_9'$ separation is 3,89 (3,2,3,4) Å; the average $C_4 \cdots C_4'$ and $C_5 \cdots C_5'$ separation is 4.46 (2, 1,1,2) Å. This particular type of distortion from planarity for the fulvalene ligand appears to be induced by the stereochemical preference of each vanadium atom for a pseudotetrahedral coordination similar to that observed for analogous $(\eta^5\text{-}C_5H_5)_2MX_2$ species[12] as well as related monofulvalene complexes of titanium[2a,b] and molybdenum which have additional bridging atoms as well as metal–metal bonding. In the present case, one coordination site of each vanadium would be occupied by the metal–metal vector and the other site by a coordinated acetonitrile ligand. The mean planes of the two five-membered rings which are η^5-bonded to a given vanadium atom of the dication intersect in an average dihedral angle of 140.8 (-,9,9,2)°. Although the 3.329 (4) Å V–V separation in **2** is significantly longer than the ~2.6 Å value generally expected for a single-order metal–metal bond involving first transition series metals [a V–V bond length of 2.462 (2) Å has, in fact, been observed[13] in $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$], it is significantly shorter than the 3.984 (4) Å Fe···Fe separation found in bis(fulvalene)diiron[14] and the 4.163 (6) Å Ni···Ni separation in bis(fulvalene)dinickel.[7] The observed structure for the dication presumably represents the best compromise between a shorter and more normal metal–metal bond and planar fulvalene ligands. Although the steric factors responsible for metal–metal bond elongation in the dication are entirely different, the observed V–V separation is quite similar to the formally single-order metal–metal bonds in the following "sterically-crowded" dinuclear complexes: $[(\eta^5\text{-}C_5H_5)(CO)_2(P(OCH_3)_3)Cr]_2$, 3.343 (3) Å Cr–Cr;[15] $[(\eta^5\text{-}C_5H_5)(CO)_3Cr]_2$, 3.281 (1) Å Cr–Cr;[16] and $[(\eta^3\text{-}C_3H_5)(CO)_3Fe]_2$, 3.138 (3) Å Fe–Fe.[17]

Thus the structural data are consistent with a significantly elongated single-order metal–metal bond in the dication which is undoubtedly due to the constraints of the bridging ligands. Such a bond would produce a seventeen-electron valence-shell electronic configuration for each vanadium atom, in agreement with the magnetic susceptibility data. The presence of a "stretched" (and presumably weakened) metal–metal bond, as well as two electron-deficient metal centers, would seem to indicate an unusually rich chemistry for this dication. The cis disposition of ligands with respect to the metal–metal axis in the bent metallofulvalene complex[18] suggests that reactions of small molecules at both metal centers could take place in either a concerted or sequential manner. These features in both the planar and bent derivatives may lead to new kinds of stoichiometric and catalytic transformations, which are quite different from those of the "parent" metallocenes.

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(11) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

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from the approximately coplanar disposition found in the cis isomer, and significantly lengthening the metal-metal distance. This suggests that metal-metal bonding may dictate the conformation in bent bis(fulvalene)-dimetal complexes apart from any possible electronic stabilization from coplanar fulvalene ligands.

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On the Photoassisted Decomposition of Water at the Gas-Solid Interface on TiO_2

Sir:

The catalytic nature of the now well-documented photoassisted decomposition of water in photoelectrochemical cells seems to be an established fact, at least on several stable anode materials such as TiO_2 or the alkaline-earth titanates.[1,2] The amount of gaseous products produced greatly exceeds that which might come from the decomposition (if any) of the surface layers of the electrode. High quantum efficiencies can be achieved and no poisoning of the reaction seems to occur, even after long reaction times.

On the other hand, the catalytic nature of the photoassisted decomposition of water at the gas-solid (GS) interface on simple catalysts, such as pure or doped TiO_2, as reported by Schrauzer and Guth,[3] has yet to be established. The efficiency was found much lower than in the photoelectrochemical devices and the reaction actually stopped after a few hours. These authors suggested that this may have been caused by catalysis of the reverse reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. This could indeed have been responsible because they used small static reactors (200 mg of catalyst in 38-mL capacity vessels).

We have, therefore, studied the photodecomposition of H_2O over TiO_2 in a flow system in order to remove the reaction products from the catalyst completely. Helium, purified by passage over charcoal at liquid nitrogen temperature, was saturated with H_2O at room temperature and flowed over the catalyst (50 cm^3 (NTP)/min) for periods up to 6 h. The catalyst (500 mg of anatase; 11.2 m^2 g) was spread uniformly on a quartz optical plate of area 5 cm^2 which made up the bottom of a flask which was joined by a standard taper joint to a vacuum-tight flow system. The TiO_2 could be illuminated from below with white light from a 1000-W xenon lamp during the test periods. The exhaust flow was first dried by passing through a liquid N_2 trap and any H_2 or O_2 was subsequently trapped downstream on activated 5A molecular sieve at this temperature. The trapped gases could be released and analyzed by mass spectrometry. The anatase was pretreated in situ at 1000 °C in flowing O_2 for 1 h (and consequently partially converted into rutile); it was cooled to 25 °C in wet He. This treatment had been recommended by Schrauzer and Guth as the most efficient for their purposes. Only traces of H_2 were detected, even after 6 h of running in UV light. The O_2 could not be detected unambiguously because of the spectrometer background at m/e 32, but certainly a substantial amount (several monolayers) could not have been missed.

We also have studied the hydrogen oxidation reaction over TiO_2, $BaTiO_3$, and $SrTiO_3$ in a static recirculation system.[4] The thermal reaction rate was found to be too slow at 25 °C by at least one order of magnitude ($<10^{-7}$ mol g^{-1} h^{-1}) to support the assumption that an equilibrium was reached in the experiments of Schrauzer and Guth, i.e., with hydrogen and oxygen partial pressures of the order of, or <1 Torr and saturating partial pressures of water. Moreover, no rate enhancement by light was found on any of these materials from 400 °C down to room temperature, although enhancement was found for CO oxidation under similar conditions with these systems.

These observations cast serious doubt about the catalytic nature of the process discovered by Schrauzer and Guth. From the particle size given for the TiO_2 sample which they used (2 μ), the specific surface area of the powder may be estimated as $\sim$1 m^2 g^{-1}. Thus, the maximum amounts of H_2 and O_2 observed (5.0×10^{18} and 2.5×10^{18} molecule g^{-1}, respectively) were of the same order as that expected for the photodecomposition of the hydroxylated surface layer[5] of the material (10^{19} OH m^{-2}).

Shrauzer and Guth also showed that hydrogen evolution was inhibited by N_2 in the gas phase and that NH_3 and N_2H_2 were produced instead of H_2, and in higher yields, especially on the iron-doped samples. Assuming again a specific surface area of the order of 1 m^2 g^{-1}, their highest yield would correspond to about seven monolayers of OH groups. A true surface area determination will be necessary, however, to make these considerations quantitative.

Another thermodynamically "uphill" reaction, namely the reaction of H_2O and CO_2 to form CH_4, has recently been shown to be photoassisted on a $SrTiO_3$-Pt sandwich.[6] Remarkably, in this case also, the reaction is poisoned when an equivalent monolayer of methane has been produced.

In contrast to these low yields, the photoassisted decomposition of water at the liquid-solid (LS) interface in TiO_2-Pt electrochemical cells occurs with typical rates of $\sim 3 \times 10^{19}$ H_2O molecules decomposed/h on a TiO_2 single-crystal electrode of area $\sim$1 cm^2.[1,2] This corresponds to a turnover number for each OH group on the electrode surface of the order of 6×10^4/h, i.e., more than four orders of magnitude higher than at the GS interface.

This large difference in turnover numbers deserves special comment. A fundamental difference between the LS and GS systems is that in the former O_2 and H_2 are produced separately at the oxide anode and at the metallic cathode, respectively, whereas in the latter both are released from the oxide surface. In both types of experiments, however, the primary process going on upon absorption of light in the surface layers may be expected to be the same, i.e., generation of an electron-hole pair, followed by trapping of some of the free carriers.

The following chemistry is written, not because we have firm conviction that it is unique and entirely correct, but rather because it affords a rationale which provides interesting food for thought. For instance, the carriers may be trapped by

$$p^+ + OH^-_{surf} \rightarrow OH\cdot_{surf} \qquad (1)$$

$$e^- + Ti^{4+} \rightarrow Ti^{3+} \qquad (2)$$

Both the participation of surface OH^- groups as hole traps and the identification of Ti^{3+} ions in various environments as donor centers conferring n-type conductivity have been widely proposed. Band to band transition and charge trapping according the eq 1 and 2 could be described together in an equivalent manner.

$$Ti^{4+}\text{-}OH^- \xrightarrow{h\nu} Ti^{3+}\text{-}OH\cdot \qquad (3)$$

The right-hand member of this equation provides on adequate center for further reaction or for electron-hole recombination.

In the photoelectrochemical (LS) devices, conduction

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