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Figure 1. Model in perspective of the $O_3Nb_2(TPP)_2$ molecule. The phenyl rings of the tetraphenylporphinato ligands have been omitted for clarity. The angles at oxygen are $Nb_1O_1Nb_2 = 94.8$ (3)°, $Nb_1O_2Nb_2 = 84.6$ (3)°, and $Nb_1O_3Nb_2 = 89.2$ (3)°.

## Remarkably Different Structures of Two Metalloporphyrins Containing $M_2O_3^{4+}$ Units

Sir:

We wish to report the molecular stereochemistry of two oxometalloporphyrins which, although they possess the same molecular formula, $[O_3M_2(TPP)_2]$,[1] $(M = Mo^V, Nb^V)$, have remarkably different structures. Synthetic methods for the preparation of oxomolybdenum(V) porphyrins were originally reported by Fleischer[2] and subsequently by Buchler and Rohbock.[3] The latter workers also reported oxometalloporphyrin derivatives with niobium(V), tungsten(V), and rhenium(V).[3,4] Niobium(V) porphyrins have also been recently reported by Guilard et al.[5] All workers reported, inter alia, derivatives with empirical formula $O_3M_2P_2$, where P is either OEP[1] or TPP. The structure suggested for these complexes, when a structure was proposed, contains a linear five-atom grouping, O=M—O—M=O, with two terminal M=O groups and a single bridging oxygen. This structure is indeed correct for the molybdenum(V) derivative but is not correct for the niobium(V) derivative

$O_3Nb_2(TPP)_2$ and $O_3Mo_2(TPP)_2$ were prepared following procedures given by Rohbock[6] for the preparation of the analogous OEP complexes. Crystals of $O_3Nb_2(TPP)_2$ were obtained from $CHCl_3$ and $O_3Mo_2(TPP)_2$ from $CHCl_3$-xylene. Crystal data and refinement results are as follows: $Nb_2O_3N_8C_{88}H_{56}\cdot CHCl_3$, monoclinic; $a = 10.765$ (5), $b = 24.913$ (6), $c = 29.332$ (8) Å; and $\beta = 112.30$ (2)°; $\rho_{calcd} = 1.43$, $\rho_{obsd} = 1.44$ g/cm³; $Z = 4$; space group Cc; $R = 0.063$ and $R_2 = 0.073$;[7] 5748 unique data $(F_o > 3\sigma(F_o), 2\theta < 58.7°)$; $Mo_2O_3N_8C_{88}H_{56}\cdot(C_8H_{10})\cdot(4CHCl_3)$, monoclinic; $a = 18.211$ (2), $b = 19.309$ (3), $c = 28.989$ (3) Å; $\beta = 115.59$ (1)°; $\rho_{calcd} = 1.47$, $\rho_{obsd} = 1.42$ g/cm³; $Z = 4$; space group $C2/c$; $R = 0.057$ and $R_2 = 0.089$; 7742 unique data $(F_o > 3\sigma(F_o), 2\theta < 54.9°)$. Intensity data were collected on a Syntex P1 diffractometer with graphite-monochromated Mo Kα radiation using ω-scanning. Tables of atomic coordinates are available; see paragraph at end of paper regarding supplementary material.

The molecular stereochemistry and bond parameters of the coordination group of the two complexes are displayed in Figures 1 and 2. Bond parameters of the core are in close agreement with those observed for other porphyrins.[8] As is clearly seen in Figure 1, the two niobium(V) porphyrin moieties are joined together by not just one bridging oxo ligand but by three. Thus, each niobium atom is seven-coordinate. Only one of the bridging oxo ligands forms a nearly symmetric bridge; the other two bridges are quite asymmetric with each niobium closely associated with a different oxygen atom of the pair of asymmetric oxo bridges.[9] The molecular stereochemistry of $O_3Mo_2(TPP)_2$ (Figure 2), however, conforms to the previously suggested structure with two terminal Mo=O groups and a single oxo bridge. Thus, each molybdenum atom is six-coordinate. The molecular stereochemistry of the tung-
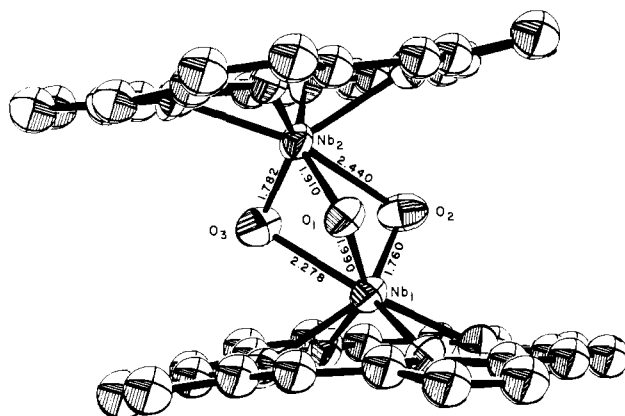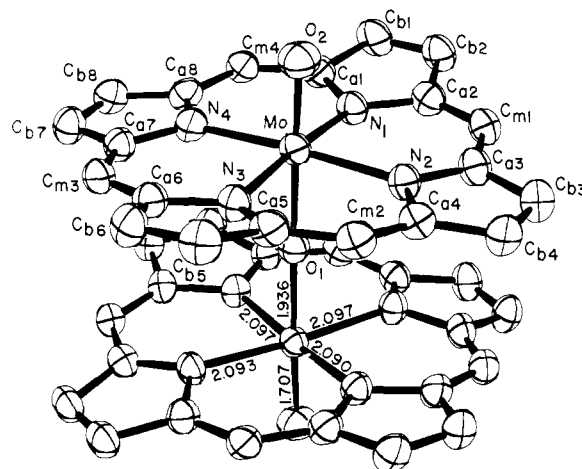
Figure 2. Model in perspective of the $O_3Mo_2(TPP)_2$ molecule. The phenyl rings of the ligand have been omitted for clarity. The crystallographically required twofold axis passes through O_1 approximately parallel to the porphyrin cores. The angles between the twofold axis and the $Mo-N_4$ and $Mo-N_1$ vectors are 15 and 75°, respectively. The $Mo-O_1-Mo$ angle is 178.63 (6)° and O_2MoO_1 is 178.2 (2)°.

sten(V) and rhenium(V) analogues is probably that of the molybdenum complex.[10]

The average Nb–N distance is 2.246 (21) Å;[11] the average NNbN angle is 78.4°. Each niobium is displaced 1.01 Å out of the mean plane of the porphinato nitrogens. The distance between the two niobium(V) atoms is 2.872 (1) Å. The two porphinato planes are not quite parallel; the dihedral angle between them is 5.2°. The dihedral angles between the oxygen atom plane and porphinato cores are 3.4 and 3.1°. The two porphinato rings have a "slipped" configuration with respect to each other, the angles between the normals to the ring passing through a niobium(V) atom and the Nb–Nb vector are 18 and 21°.

The average Mo–N distance is 2.094 (3) Å and the molybdenum(V) atom is displaced 0.09 Å ot of the mean plane of the porphyrin nitrogens toward the terminal oxo ligand. The terminal Mo=O groups are trans to the Mo–O–Mo bridge, all other complexes containing a $Mo_2O_3^{4+}$ unit have the Mo=O terminal groups cis with respect to the Mo—O—Mo bridge.[12] The Mo—O—Mo bridge is essentially linear; the angle is 178.63 (6)°. The Mo=O (terminal) bond distance of 1.707 (3) Å and the Mo—O (bridge) bond distance of 1.936 (3) Å are slightly longer than the corresponding distances observed in the other $Mo_2O_3^{4+}$ binuclear complexes.[12] The slight lengthening of the two types of bonds is presumably the result

of the mutual trans influence of the oxo ligands. The paramagnetism of $O_3Mo_2(TPP)_2$,[2,6,13] as contrasted to the diamagnetism of the other $Mo_2O_3^{4+}$ complexes, is easily understood from the structure differences. If the Mo=O (terminal) bond fixes the z direction and d_{xy} is the populated 4d orbital,[12a] overlap of the d_{xy} orbitals between the Mo atoms is inhibited in $O_3Mo_2(TPP)_2$ but not in the other $Mo_2O_3^{4+}$ complexes. The two skeletons are approximately staggered with NMoMo'N' dihedral angles of ~30 and 60°.[14] The porphyrin interplanar separation in the Mo derivative is ~3.8 and ~4.9 Å in the Nb complex.

The large difference in the structures of $O_3Mo_2(TPP)_2$ and $O_3Nb_2(TPP)_2$ seems to result from the difference in the affinity of the two metals for the porphinato ligand. The structure observed for the Mo complex leads to strong interaction of each metal atom with its porphinato ligand and two oxo ligands. This arrangement concomitantly requires an energetically demanding radial expansion of the porphinato core (Ct···N = 2.092 Å),[17] a large number of tight O···N contacts, and a rather close intramolecular porphyrin interplanar spacing. The configuration of the Nb complex allows strong interaction of each metal atom with two oxo ligands and a weaker one with the third but also requires a decreased interaction of the metal atoms with the porphinato ligands. The decreased interaction is presumably partly counterbalanced by diminished radial strain of the porphinato ring (Ct···N = 2.006 Å), a smaller number of tight O···N contacts, and a substantially larger intramolecular interplanar spacing. We note that these different interactions of the metal atom with the porphinato ligand are also observed in the respective monomeric complexes. Thus in six-coordinate porphinatomolybdenum(V) derivatives,[18] the Mo atom is nearly centered in the prophinato plane, while in seven-coordinate acetatooxotetraphenylporphinatoniobium(V)[19] the Nb atom is displaced 1.0 Å out-of-plane and the oxo and the bidentate acetato ligands are on the same side of the porphinato plane.

Supplementary Material Available: Tables of atomic coordinates (8 pages). Ordering information is given on any current masthead page.

References and Notes

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(9) Ignoring the small differences in the pairs of Nb–O bonds (Nb$_1$–O$_1$, Nb$_2$–O$_1$; Nb'$_1$–O$_2$, Nb$_2$–O$_3$; Nb$_1$–O$_3$, Nb$_2$–O$_2$), the molecule has C_2 symmetry. A recently obtained modification of $O_3Nb_2(TPP)_2$ has a crystallographically required twofold axis. The IR spectra of the two are essentially identical. $O_3Mo_2(TPP)_2$ has a strong Mo=O stretch at 905 cm^{-1}, the Nb—O stretches are weaker and at lower frequencies.
(10) Indeed, crystals of $O_3Re_2(TPP)_2$ are isomorphous with $O_3Mo_2(TPP)_2$.
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(13) Measurements on our crystalline samples gave $\mu = 1.7\ \mu_B$ (per Mo) at room temperature.
(14) Similar orientation of the two porphyrin cores are observed in O(FeTPP)$_2$[15] and N(FeTPP)$_2$.[16]
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Mechanism of Reductive Elimination. 2.[1] Control of Dinuclear vs. Mononuclear Elimination of Methane from cis-Hydridomethyltetracarbonylosmium

Sir:

A general picture of the elimination of cis organic ligands from transition metal complexes must explain the rapid elimination of alkanes from almost all alkyl hydride complexes, the instability of which is particularly striking in comparison with the relative stability of dihydrido and dimethyl complexes.[2-7] This generalization is exemplified by the order of stability $Os(CO)_4(H)CH_3 \ll Os(CO)_4H_2 \ll Os(CO)_4(CH_3)_2$, to which we have called attention.[1] We have long felt the most likely explanation to be a mechanism unique to the combination of alkyl and hydride ligands.

We now report that elimination of methane from cis-$Os(CO)_4(H)CH_3$ (**1a**) to form $HOs(CO)_4Os(CO)_4CH_3$ (**2**)[3] proceeds by a dinuclear process, despite the presence of cis methyl and hydride ligands.[8-14] We further report that an external nucleophile, by intercepting an intermediate common to both reactions, can convert methane elimination from $Os(CO)_4(H)CH_3$ into a mononuclear process.

As with $Os(CO)_4H_2$,[1] the observation of the dinuclear **2** as primary decomposition product of $Os(CO)_4(H)CH_3$ (**1a**) suggests—but does not prove—that a dinuclear elimination is occurring. Fortunately, as we are dealing here with an *isolable* hydridomethyl complex,[15] the appropriate crossover experiment is feasible. Use of either CF_3COOD or CD_3OSO_2F in place of their nondeuterated analogues in the synthesis[3] of cis-$Os(CO)_4(H)CH_3$ allows preparation of $Os(CO)_4(D)CH_3$ (**1b**) and $Os(CO)_4(H)CD_3$ (**1c**), respectively.

The thermolysis of a mixture of **1b** and **1c** under a wide variety of conditions (from 10^{-2} M in methylcyclohexane to a mixture of pure liquids) yields substantial quantities of CD_4, demonstrating dinuclear elimination.[16] From quantitative analysis of the isotopically labeled methanes (CD_4, CD_3H, CDH_3, and CH_4 a primary kinetic isotope effect k_H/k_D of 1.5 ± 0.2 can be obtained. This small effect is about the same as that (k_{HH}/k_{HD} of 1.4) seen with the $Os(CO)_4H_2/Os(CO)_4D_2$ system.[1]

A control experiment, the decomposition of $Os(CO)_4(H)CH_3$ in the presence of an equivalent of CD_4, gives only CH_4 and CD_4 and confirms that the dinuclear mechanism inferred from the preceding data is correct. In order to explore the details of this mechanism, rate studies on

$$2Os(CO)_4(H)CH_3 \rightarrow CH_4 + HOs(CO)_4Os(CO)_4CH_3$$

$$(1)$$
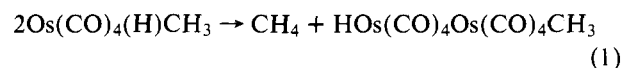
have been carried out. The rate of disappearance[17] of **1** is *first order* in **1**

$$d[Os(CO)_4(H)CH_3]/dt = -k_1[Os(CO)_4(H)CH_3]$$

with $k_1 = (1.38 \pm 0.06) \times 10^{-4}$ s^{-1} at 49 °C, invariant between 10^{-2} and 10^{-3} M initial concentration in methylcyclohexane. The rate is not particularly solvent-sensitive: $k_1 =$