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Synthesis, Structure, and Characterization of a Sulfate-Bridged Oxomolybdenum(V) Porphyrin Dimer and Related Monomers Including a Nitrate Complex

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New oxomolybdenum(V) porphyrin complexes, [MoO(tmp)($C_6H_5SO_3$)] **1**, [MoO(tpp)($C_6H_5SO_3$)] **2**, [MoO(tpp)(HSO_4)] **3**, [{MoO(tpp)}$_2$(μ-SO_4)] **4**, and [MoO(tpp)(NO_3)] **5**, were synthesized and characterized by UV-vis, IR, FAB-MS, and ESR measurements. The structures of the complexes, **1**, **4**, and **5**, were determined by X-ray crystallographic analysis. The benzenesulfonate ion in **1** and the nitrate ion in **5** coordinate to the molybdenum atom as monodentate ligands. The oxidation number of the central molybdenum ion of these complexes was confirmed to be 5+ by ESR measurements. In the dinuclear complex **4**, a sulfate ion bridges two molybdenum porphyrins. The dinuclear complex **4** exhibited spin coupling between the two molybdenum nuclei.

Molybdenum is the only heavy transition metal of known wide spread occurrence in biological systems and is found in several enzymes such as sulfite oxidase, nitrate reductase, and nitrogenase.[1] Although these enzymes contain no molybdenum porphyrin complexes, the products formed by the reactions with oxoanions such as a sulfate ion and a nitrate ion are of great interest. Practically, in molybdenum porphyrin systems, intensive studies[2,3] showed that molybdenum(IV, V) porphyrins underwent reactions with some oxoanion analogues such as $O_2{}^-$, $O_2{}^{2-}$, and CH_3O^- to give singular complexes of oxoperoxo(porphyrinato)molybdenum(V),[4] diperoxo(porphyrinato)molybdenum(VI),[5] and (methoxo)porphyrinatomolybdenum(V),[6] respectively. A recent study also revealed that a molybdenum(IV) porphyrin having a bulky porphyrin ring gives a molybdenum(VI) porphyrin dioxygen complex on reversible reaction with molecular oxygen at room temperature.[7] However, no porphyrinato(sulfato)molybdenum complexes and (nitrato)porphyrinatomolybdenum complexes have been synthesized yet, though other sulfate complexes having no porphyrin rings, such as $K_4[Mo_2(SO_4)_4]$ in which four sulfate ions bridge two molybdenum atoms[8] and $[\{(SO_4)Mo(O)(\mu\text{-}S)_2Mo(O)(SO_4)\}_2(\mu_4\text{-}SO_4)]^{6-}$ where a sulfate ion (μ_4-SO_4^{2-}) bridges four molybdenum atoms,[9] have been characterized.

From these considerations, the authors were inspired to clarify the coordination fashion of prospective porphyrinato(sulfato)molybdenum complexes and a (nitrato)porphyrinatomolybdenum complex. In the present work, mononuclear complexes such as [MoO(tmp)($C_6H_5SO_3$)] **1**, [MoO(tpp)($C_6H_5SO_3$)] **2**, and [MoO(tpp)(HSO_4)] **3**, a sulfate-bridged dinuclear complex [{MoO(tpp)}$_2$(μ-SO_4)] **4**, and [MoO(tpp)(NO_3)] **5**, were synthesized and characterized.[10] Among these complexes, **1**, **4**, and **5** were also characterized crystallographically.

Results and Discussion

All the sulfate complexes and the nitrate complex were characterized by spectroscopic measurements. ESR measurements indicated that all these oxoanion-coordinated complexes have molybdenum(V) oxidation states, as described later. The structures of **1**, **4**, and **5** were determined by X-ray crystallography.

Crystal Structure of [MoO(tmp)($C_6H_5SO_3$)]·2$C_6H_5CH_3$ (1·2$C_6H_5CH_3$). The X-ray analysis disclosed that the crystal contains toluene molecules as a crystallizing solvent. The $C_6H_5SO_3$ group coordinates to Mo atom through an O atom at the position *trans* to the axial oxo ligand and is disordered in two positions around the coordinated oxygen atom. These disordered groups are designated as group A or group B. Figure 1 shows the structure with group A. Selected bond lengths and bond angles are given in Table 1. The four mesityl groups which are omitted in Fig. 1 are perpendicular to the porphyrin plane (78.4—88.2° from the mean 24-atom porphyrin core). The plane of the benzene ring of the $C_6H_5SO_3$ group faces the porphyrin plane. The central Mo atom is displaced toward the axial oxo ligand by 0.38 Å from the mean plane of the 24 atom core and by 0.29 Å from that of the four pyrrole nitrogen atom core, as shown in Table 2. This feature is in contrast to the displacement of the Fe and Mn atoms toward the HSO_4 group in [Fe(tpp)(HSO_4)][12]

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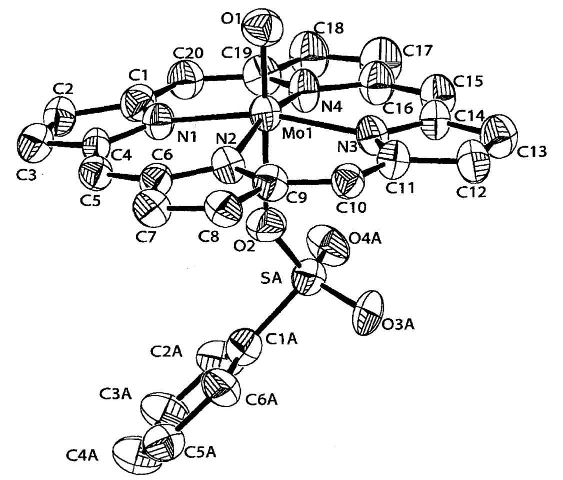

Fig. 1. Molecular structure and atom labeling of [MoO(tmp)($C_6H_5SO_3$)] **1** with a group A. The mesityl groups are omitted for clarity.

and [Mn(tpp)(HSO_4)].[13] The reverse displacement of the Mo atom toward the oxo atom may be attributed to the strong coordination of the axial oxo atom in molybdenum complexes. The bond distances of Mo=O and Mo–N_{av} are 1.66 and 2.09 Å, respectively, which are similar to those of other oxomolybdenum(V) tetraphenylporphyrins such as [MoO(tpp)NCS] (1.673, 2.086 Å),[14] [MoO(ttp)F] (1.677, 2.089 Å),[14] and [MoO(tpp)Cl] (1.714, 2.118 Å).[15] On the contrary the distance of Mo–O(benzenesulfonato) (2.18 Å) is significantly long compared to those of [$\{Mo^VO(tpp)\}_2(\mu$-O)] (Mo–O(μ-O) = 1.936 Å)[16] and [Mo^VO(dptbtmp)(OCH_3)] (Mo–O(methoxo) = ca. 1.89 Å).[17]

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

	[MoO(tmp)($C_6H_5SO_3$)] **1**		
Mo1–O1	1.664(7)	O1–Mo1–O2	178.4(3)
Mo1–O2	2.179(7)	O1–Mo1–N_{av}	98.0
Mo1–N_{av}	2.09	O2–Mo1–N_{av}	81.1
S(A)–O2	1.496(9)	O2–S(A)–O3(A)	110.3(7)
S(A)–O3(A)	1.461(13)	O2–S(A)–O4(A)	111.3(7)
S(A)–O4(A)	1.425(13)	O2–S(A)–C(1A)	103.3(8)
S(A)–C(1A)	1.764(22)	O3(A)–S(A)–O4(A)	118.2(8)
S(B)–O2	1.456(10)	O3(A)–S(A)–C(1A)	106.3(9)
S(B)–O3(B)	1.437(21)	O4(A)–S(A)–C(1A)	106.1(9)
S(B)–O4(B)	1.438(20)	Mo1–O2–S(A)	143.2(5)
	[$\{MoO(tpp)\}_2(\mu - SO_4)$] **4**		
MoA–MoB	6.630(3)	O1A–MoA–O2A	178.3(5)
MoA–O1A	1.676(14)	O1A–MoA–N_{av}	97.3
MoA–O2A	2.182(12)	O2A–MoA–N_{av}	82.7
MoB–O1B	1.640(12)	O2B–MoB–O1B	175.8(5)
MoB–O2B	2.147(12)	O2B–MoB–N_{av}	84.1
MoA–N_{av}	2.09	O1B–MoB–N_{av}	96.0
S1–O2A	1.515(12)	O2A–S1–O3	111.2(9)
S1–O3	1.441(15)	O2A–S1–O4	108.8(8)
S1–O4	1.457(14)	O2A–S1–O2B	101.7(7)
S1–O2B	1.547(13)	O3–S–O4	115.3(9)
		O3–S1–O2B	109.0(8)
		O4–S1–O2B	110.0(9)
		MoA–O2A–S1	133.6(7)
		MoB–O2B–S1	134.6(6)
	[MoO(tpp)(NO_3)] **5**		
Mo1–O1	1.671(2)	O1–Mo1–O2	176.5(1)
Mo1–O2	2.243(2)	O1–Mo1–N1	98.2(1)
Mo1–N1	2.085(3)	O1–Mo1–N2	97.8(1)
Mo1–N2	2.093(3)	O1–Mo1–N3	99.3(1)
Mo1–N3	2.089(3)	O1–Mo1–N4	99.2(1)
Mo1–N4	2.091(3)	Mo1–O2–N5	135.5(2)
		O2–N5–O3	119.3(3)
		O2–N5–O4	120.6(3)
		O3–N5–O4	119.2(3)

Crystal Structure of [$\{MoO(tpp)\}_2(\mu$-$SO_4)]\cdot 2CH_2Cl_2\cdot C_5H_{12}\cdot H_2O$ (4$\cdot 2CH_2Cl_2\cdot C_5H_{12}\cdot H_2O$). The elemental analysis confirmed that the crystals of **4** contain two dichloromethane molecules, one *n*-pentane, and one water. Thus the complex is formulated as **4**$\cdot 2CH_2Cl_2\cdot C_5H_{12}\cdot H_2O$. A sulfate ion coordinates to two molybdenum atoms through different oxygen atoms as shown in Fig. 2(a). The overall structure of the dinuclear complex is very similar to those of [$\{Fe(tpp)\}_2(\mu$-$SO_4)$][18] and [$\{Mn(tpp)\}_2(\mu$-$SO_4)$].[13] The dihedral angle between the two porphyrin cores of **4** (19.8 and 21.4° between the mean planes defined by the 24-atom core and by the 4N atom core, respectively) is not different from those

Table 2. Structure Comparison of Oxomolybdenum Porphyrins

Complex	Mo=O	Mo–N_{av}	Mo-24 atom plane	Mo–A(L)	Mo–A(L)/Å calcd
	Å	Å	Å	Å	from ionic radii[g)]
[MoO(ttp)][a)]	1.656(6)	2.110(6)	0.7344(8)		
[MoO(ttp)F][b)]	1.677(12)	2.089(3)	0.155(9)[f)]	1.967(9)	1.94
[MoO(ttp)Cl][c)]	1.714(3)	2.118(3)	0.390[f)]	2.494	2.42
[MoO(ttp)NCS][b)]	1.673(3)	2.086(5)	0.282(4)[f)]	2.257(4)	(2.08)[h)]
[MoO(dptbtmp)(OCH_3)][d)]	1.80(1)	2.11(4)	0.092	1.89(1)	1.99
[$\{MoO(tpp)\}_2(\mu$-O)][e)]	1.707(3)	2.094(3)	0.01	1.936(3)	1.99
[MoO(tmp)($C_6H_5SO_3$)] **1**	1.664(7)	2.09	0.381	2.179(7)	1.99
[$\{MoO(tpp)\}_2(\mu$-$SO_4)$] **4** (core A)	1.676(14)	2.09	0.27	2.182(12)	1.99
(core B)	1.640(12)	2.09	0.23	2.147(12)	1.99
[MoO(tpp)(NO_3)] **5**	1.671(2)	2.09	0.39	2.243(2)	1.99

a) Ref. 11. b) Ref. 14. c) Ref. 15. d) Ref. 17. e) Ref. 16. f) Displacement of Mo ion from the mean 4N-atom porphyrin core. g) Calculated from ionic radii reported in Ref. 30. h) Calculated from the ionic radius (1.32 Å) of N^{3-}.

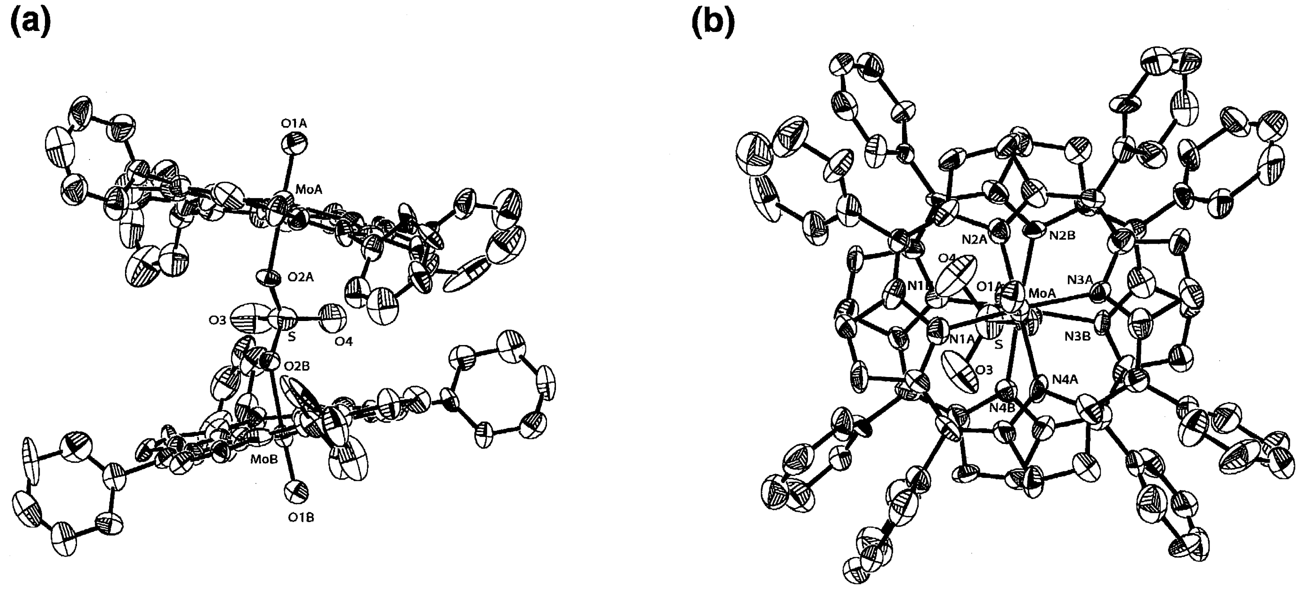

Fig. 2. Molecular structure of $[\{\mathrm{Mo^{V}O(tpp)}\}_2(\mu\text{-}\mathrm{SO_4})]$ **4**: (a) side view, (b) top view.

of the iron (24°) and manganese (22°) complexes. The location of the two molybdenum atoms and of the two porphyrin planes is not equivalent, at least in the crystalline state. The two Mo atoms are lifted by 0.27 and 0.23 Å toward the axial oxo ligands from the 24-atom mean plane formed by the independent porphyrin cores, denoted by core A and core B respectively. This difference leads to a relatively small value (6.16 Å) of the distance between the centers formed by the two porphyrin cores, compared to the iron (ca. 6.91 Å) and manganese (6.72 Å) dinuclear complexes. The twist angle of N1A–MoA–MoB–N1B is 23.0°, which is supposed to be the result of the mutual steric hindrance between the phenyl groups of the two porphyrins (Fig. 2(b)). The O atoms of the sulfate ions of the complex are located tetrahedrally to the S atoms, as expected. The bond distances of S–O(coord.) (av. 1.53 Å) are a little longer than those of S–O(uncoord.) (av. 1.45 Å). The displacements of the molybdenum atoms (0.27 and 0.22 Å from the mean 4N planes) and the bond distances of Mo=O (1.68 and 1.64 Å) and Mo–O(sulfate) (2.18 and 2.15 Å) are comparable to those of $[\mathrm{MoO(tmp)(C_6H_5SO_3)}]$ **1**, as shown in Tables 1 and 2.

Crystal Structure of $[\mathrm{MoO(tpp)(NO_3)}]\cdot\mathrm{CH_2Cl_2}$ (5·$\mathrm{CH_2Cl_2}$). The molecular structure of **5** is shown in Fig. 3. The Mo atom displaces toward the oxo ion by 0.32 and 0.39 Å from the mean plane of the four porphyrin nitrogen atoms and from that of the 24 atoms, respectively. The Mo=O bond distance is 1.67 Å, which is almost the same as those of **1** and **4**. The nitrate ion coordinates to the molybdenum atom as a monodentate ligand as in $[\mathrm{Mn(tpp)(NO_3)}]$,[19] while in $[\mathrm{Fe(tpp)(NO_3)}]$[20] or $[\mathrm{Co(por)(NO_3)}]$[21] the nitrate ion coordinates as a didentate ligand.[22] The Mo–O-($\mathrm{NO_3}$) distance (2.24 Å) is longer than the Mo=O bond and still longer than that of Mo–O($\mathrm{OCH_3}$) (1.89 Å) in $[\mathrm{Mo^{V}O(dptbtmp)(OCH_3)}]$,[17] as well as the Mo–O(sulfate) distance in $[\mathrm{Mo^{V}O(tmp)(C_6H_5SO_3)}]$ **1** (2.174 Å) and the Mo–O(sulfate) distance in $[\{\mathrm{Mo^{V}O(tpp)}\}_2(\mu\text{-}\mathrm{SO_4})]$ **4** (2.18 and 2.15 Å). The angle of O=Mo–O in **5** is almost 180°, similar to other six coordinate molybdenum(V) porphyrin complexes. The O–N–O bond angles in the nitrate ion are almost 120°, as observed in $[\mathrm{Mn(tpp)(NO_3)}]$[19] and $[\mathrm{Fe(tpp)(NO_3)}]$.[20]

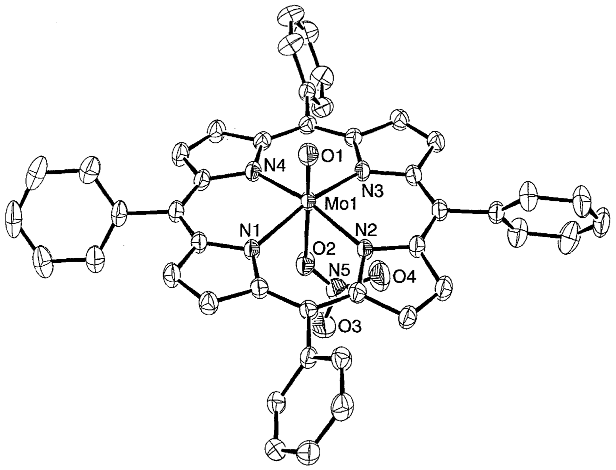

Fig. 3. Molecular structure of $[\mathrm{MoO(tpp)(NO_3)}]$ **5**.

ESR Spectra. Analysis of the ESR signals confirmed that the oxidation number of the central molybdenum of all these five complexes including the dinuclear complex **4** is 5+ ($\mathrm{d^1}$), as shown in Fig. 4. However, there were subtle differences in the ESR signals in these complexes. In the mononuclear complexes **1**, **2**, **3**, and **5**, each of the ESR spectra in $\mathrm{CH_2Cl_2}$ or toluene consists of a strong central line around $\overline{g} = 1.97$ and six weak lines with almost the same intensity due to the molybdenum nucleus with $I = 0$ (natural abundance, 74.5%) and $^{95,97}\mathrm{Mo}$ nuclei with $I = 5/2$ (natural abundance, 25.5%, $A_{\mathrm{Mo}} = 4.8$—5.1 mT, ca. $46\times10^{-4}\,\mathrm{cm^{-1}}$), respectively, as shown in Fig. 4(A). This is characteristic of molybdenum(V) ($\mathrm{d^1}$) porphyrins, as observed in other Mo(V) complexes such as $[\mathrm{Mo^{V}O(tpp)X}]$ ($\mathrm{X^-}=\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NCS^-}$).[2] The central strong line in $[\mathrm{MoO(tpp)(NO_3)}]$

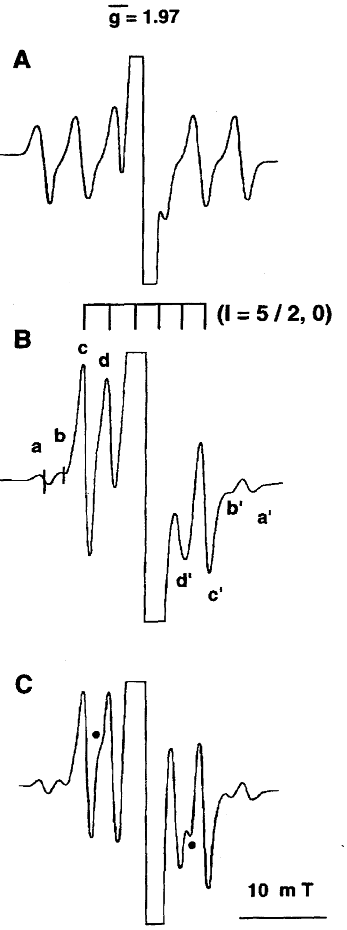

Fig. 4. ESR spectra of **5** in dichloromethane (**A**) and **4** (**B** at 25 °C and **C** at 110 °C) in toluene. ● denotes additional signals due to a coupling between $I = 5/2$ and $I = 5/2$ at 110 °C.

5 clearly splits into nine lines by coupling of the Mo nucleus ($I = 0$) with four nitrogen nuclei ($I = 1$).[2] The splits in the complexes, **1**—**3**, are not so clear, due to broadening of the lines. This can be explained by the restricted orientation of the coordinated axial ligands, HSO_4^- and $C_6H_5SO_3^-$.

Different from the ESR signals of **1**, **2**, **3**, and **5** described above, the dinuclear complex **4** in toluene has a rather complicated signal, as shown in Fig. 4(B). The strong central signal (Mo, $I = 0$) gave no precise splittings, and the signals due to ^{95,97}Mo nuclei were not so simple as the mononuclear complexes. In general, when there exist two unpaired electrons in a molecule such as nitroxybiradicals, the hyperfine splitting structure is affected by the exchange interactions between the two electrons to give a hyperfine (hfc) coupling constant which is half of that in a one electron system.[23] Practically, molybdenum(V) porphyrin dinuclear complexes formed by bridging with 1,5-naphthalenediol showed signals having almost half the hyperfine coupling constant ($A_{Mo} = 21.0\times10^{-4}$ cm^{-1}) of general oxomolybdenum porphyrin mononuclear complexes ($A_{Mo} \approx 46\times10^{-4}$ cm^{-1}), which is characteristic of the species having rapid spin couplings between two molybdenum nuclei.[24]

The ESR signal of the dinuclear complex **4** solution revealed this characteristic pattern of spin couplings between $I = 5/2$ and $I = 0$ around $\bar{g} = 1.97$ (**c**, **d**, **c**′, and **d**′ in Fig. 4(B)), and $I = 5/2$ and $I = 5/2$ (**a**, **b**, **a**′, and **b**′. The other signals caused by this coupling hide in the large signals of **c**, **d**, **c**′, and **d**′), in the two molybdenum nuclei, i.e., the solution shows a relation in signal-band width, with ΔHab (ca. 27×10^{-4} cm^{-1}) $\approx \Delta H$cd $\approx \Delta1/2H$ac $\approx \Delta1/3H$dd′, at 25 °C. The hyperfine splitting due to the coupling between $I = 5/2$ and $I = 0$ of the two Mo nuclei in **4** was estimated to be about 2.97 mT (27.3×10^{-4} cm^{-1}). Although the value is a little larger than half of the general hfc values (4.8—5.0 mT, ca. 46×10^{-4} cm^{-1}) of mononuclear complexes, the spectral feature of **4** demonstrates essentially that two unpaired electrons in two Mo(V) are rapidly exchanged across the bridging sulfate ion. When the temperature of the solution of **4** was raised from 25 to 110 °C, the hidden signals, denoted by ● in Fig. 4(C), appeared between **c** and **d**, and **c**′ and **d**′, and the spectrum became more characteristic of spin coupling. However, even at 110 °C the spin exchange was not completed. The ESR results reveal that the spin exchange between the two Mo ions is fast but not as fast as the 1,5-naphthalelenediol-bridged molybdenum porphyrin dinuclear complexes.[24] This may be due to the rectangular Mo–O–S–O–Mo bridge and its rather rigid structure in the dinuclear complex **4**.

UV-visible Spectra. The Soret band of oxo(porphyrinato)molybdenum(V) would be assigned to the charge-transfer (CT) transition mixed with π–π* transitions as those assigned for manganese(III) porphyrin complexes.[25] In a series of [Mo^{V}O(tpp)X] with a simple monoanionic ligand, X, such as halide ions and NCS$^-$, the electronegativity values of the donor atoms of the axial ligands were predominantly responsible for the values of λ_{max} in the UV-vis spectra.[26] For example, the Soret bands of MoO(tpp)X in dichloromethane red-shift in the order, X = F (λ_{max} = 463 nm) < N (NCS) (488) < Cl (500) < Br (510)[26,27] which is almost the same as the decreasing order of electronegativity,[28] that is, F (4.0) > N (3.0) ≈ Cl (3.0) > Br (2.8). From this trend, the absorption maxima of the Soret bands of the present complexes having oxoanions such as a sulfate ion and a nitrate ion were expected to be around 450 nm, because the electronegativity of the coordinating atom, O, of the oxoanion and benzenesulfonato ligands (HSO_4^-, NO_3^- and $C_6H_5SO_3^-$) in this work is about 3.5. Actually, [MoO(tpp)(OCH_2CH_3)] has the Soret band at 454 nm[26] and even the dinuclear complex of [{MoO(tpp)}$_2$(μ-O)] has the band at 444 nm.[16] In addition, [MoO(dptbtmp)(OCH_3)] which has two phenyl substituents at the *meso* position of the porphyrin rings shows the Soret band at 450 nm.[17] However, all the sulfate or nitrate complexes in the present work give the Soret bands around 479—491 nm. The location of the bands in this region is similar to the [MoO(tpp)ClO_4] complex which also has the Soret band in the same region at 480 nm.[29] Thus the Soret bands of the [Mo^{V}O(tpp)(oxoacidato)] complexes deviate from the above-mentioned trend.

As shown in Table 2, the determined Mo–A(L) bond lengths (A = a coordinated atom of an axial ligand L) of [MoO(tpp)F] (1.967 Å),[14] [MoO(tpp)Cl] (2.257 Å),[15] [MoO(dptbtmp)(OCH_3)] (1.89 Å),[17] and [{MoO(tpp)}$_2$-(μ-O)] (1.936 Å),[16] in which the Soret bands are on the spectral trend, are almost the same as the respective values of 1.94, 2.42, 1.99, and 1.99 Å obtained by calculation from ionic radii.[30] On the other hand, in the [MoO(tpp)(oxo-acidato)] complexes, Mo–A(L) are relatively longer than the calculated Mo–A(L) lengths by about 0.16—0.25 Å. It seems that the deviation of the Soret bands of [Mo^{V}O(tpp)(oxo-acidato)] from the UV-vis spectral trend reflects elongation in the Mo–A(L) bond lengths.

Experimental

All solvents except toluene are reagent grade. Toluene was spectral grade. Dichloromethane was passed through a column of basic alumina (activity I) to remove stabilizer and distilled under argon prior to use. Other materials such as benzenesulfonic acid, $C_6H_5SO_3H{\cdot}H_2O$, sulfuric acid, and silver sulfate were reagent grade and were used without further purification. The dioxygen complex of [MoO(tmp)(O_2)],[7] and [MoO(tpp)Br][26] were prepared by previously reported procedures.

Synthesis of [MoO(tmp)($C_6H_5SO_3$)] 1. To 100 ml of the dichloromethane solution containing 500 mg of [MoO(tmp)(O_2)], an excess of $C_6H_5SO_3H{\cdot}H_2O$ was added with stirring. After the UV-vis absorption peak of the solution had shifted from 432 to 491 nm completely, the solution was passed through a sintered glass funnel and evaporated to dryness. The black-green solid material obtained was again dissolved in toluene. The solution was filtered to eliminate the precipitate of $C_6H_5SO_3H{\cdot}H_2O$ and evaporated. The product was washed with water, dried, and recrystallized from *n*-pentane–toluene. The complex was dried under reduced pressure (13 Pa, 0.1 Torr) at 100 °C (yield: 340 mg, 61%).

Found: C, 70.98; H, 5.62; N, 5.17; S, 3.12%. Calcd for $C_{62}H_{57}N_4O_4SMo$: (M = 1050.17); C, 70.91; H, 5.47; N, 5.34; S, 3.05%. UV-vis λ_{max} ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) in $C_6H_5CH_3$: 328 (52.0), 414 (32.7), 491 (55.7), 618 (11.7), 661 nm (8.87). MS (FAB), m/z^+ 893 ([MoO(tmp)]$^+$). IR (KBr) ν = 957 (νMo=O); 561 (νMo–O); 608, 1114, 1166, 1279 cm^{-1} ($\nu C_6H_5SO_3$). ESR spectrum shows a typical signal of a molybdenum(V) porphyrin complex having $\bar{g}$ = 1.97.[2]

[MoO(tpp)($C_6H_5SO_3$)] 2. Benzenesulfonic acid $C_6H_5SO_3H{\cdot}H_2O$ (51 mg, 0.32 mmol) was added to 100 ml of the dichloromethane solution containing [Mo^{V}O(tpp)Br] (400 mg, 0.12 mmol) and stirred for 1 d. The solution was filtered and evaporated to dryness. The resulting solid material was recrystallized from *n*-pentane–dichloromethane and then from *n*-pentane–toluene. The solid powder obtained was washed with distilled water and dried at 140 °C for 9 h under 13 Pa (yield: 91.2 mg, 83.2%).

Found: C, 67.62; H, 3.77; N, 6.36; S, 3.59%. Calcd for $C_{50}H_{33}N_4O_4SMo$: (M = 881.84); C, 68.02; H, 3.89; N, 6.35; S, 3.63%. UV-vis λ_{max} ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2 335 (46.0), 487 (49.2), 614 (9.96), 659 nm (8.03). IR (KBr) ν = 962 (νMo=O); 552 (νMo–O); 609, 1112, 1167, 1277 cm^{-1} ($\nu C_6H_5SO_3$).

[MoO(tpp)(HSO_4)] 3. The dichloromethane solution (75 ml) containing [Mo^{V}O(tpp)Br] (150 mg, 0.19 mmol) and H_2SO_4 (0.25 ml, 4.2 mmol) was stirred in the dark for 2 d. The organic layer was separated and evaporated to dryness to give the expected complex. This procedure was repeated twice for purification. The black-green complex was recrystallized from *n*-pentane–dichloromethane and dried under vacuum at 140 °C for 4 h (yield: 88.5 mg, 57.6%). This complex failed to give single crystals suitable for X-ray structure analysis. Nevertheless the structure is supposed to be analogous to that of [MoO(tmp)($C_6H_5SO_3$)] 1 because of the similarity in electronic and IR spectra between the two complexes.

Found: C, 62.69; H, 3.81; N, 6.68; S, 3.81%. Calcd for [MoO(tpp)(HSO_4)]$\cdot H_2O$: ($C_{44}H_{31}N_4O_6SMo$, 839.76); C, 62.93; H, 3.73; N, 6.67; S, 3.82%. UV-vis λ_{max} ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) in $C_6H_5CH_3$ 338 (41.9), 486 (46.0), 614 (9.32), 659 nm (7.13). UV-vis λ_{max} ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2 334 (43.2), 487 (44.4), 614 (8.92), 658 nm (7.11). IR (KBr) ν = 974 (νMo=O); 574 (νMo–O); 593, 886, 1051, 1193 cm^{-1} (νHSO_4).

[{MoO(tpp)}$_2$(μ-SO_4)] 4. The complex was synthesized in reference to the reported methods for [{Mn(tpp)}$_2$(μ-SO_4)][13] and [Mn(tpp)NO_3].[19] Preparation was performed in the dark. 80 ml of the dichloromethane solution of [MoO(tpp)Br] (80 mg) was shaken with 20 ml of an aqueous solution saturated with Ag_2SO_4 (160 mg) for 6 h. This procedure gave a white precipitate of AgBr in the aqueous layer. The organic layer was separated, dried with anhydrous Na_2SO_4, and passed through a sintered glass funnel. The filtrate was evaporated to dryness. Recrystallization from *n*-pentane–dichloromethane gave a dark green powder (yield: 28 mg, 36%). The solid complex contained CH_2Cl_2 molecules, the number per complex varied with the preparation procedures.

Found: C, 66.64; H, 4.32; N, 6.94; S, 1.72%. Calcd for [{MoO(tpp)}$_2$(μ-SO_4)]$\cdot CH_2Cl_2 \cdot C_5H_{12}$: ($C_{94}H_{70}Cl_2N_8O_6SMo_2$, 1702.49); C, 66.32; H, 4.15; N, 6.58; S, 1.88%. UV-vis λ_{max} ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2 333 (93.9), 479 (87.5), 616 (16.2), 660 nm (14.1). MS (FAB), m/z^+ 1547 ([{MoO(tpp)}$_2$(SO_4)]$^+$), 821 ([MoO(tpp)(SO_4H)]$^+$). IR (KBr) ν = 972 (νMo=O); 571 (νMo–O); 619, 882, 903, 1120 cm^{-1} (νSO_4). The dark-green single crystals of [{MoO(tpp)}$_2$(μ-SO_4)]$\cdot 2CH_2Cl_2 \cdot C_5H_{12} \cdot H_2O$ suitable for X-ray structure analysis were obtained by the diffusion of *n*-pentane into the dichloromethane solution of the powder.

[MoO(tpp)(NO_3)] 5. $AgNO_3$ (34 mg, 0.2 mmol) was added to the dichloromethane (5 ml) solution of [MoO(tpp)Br] (40.2 mg, 0.05 mmol) and stirred for 4 h in the dark. The insoluble materials such as unreacted $AgNO_3$ and AgBr were filtered off. The solution was evaporated to give a green solid material which was recrystallized from *n*-pentane–dichloromethane. The solid was dried for 1.5 h in vacuo at room temperature followed by heating at 120 °C for another 3 h in vacuo (yield: 28.7 mg, 73%).

Found: C, 66.40; H, 3.89; N, 8.64%. Calcd for $C_{44}H_{28}N_5O_4Mo$: (M = 786.18) C, 67.20; H, 3.56; N, 8.90%. UV-vis λ_{max} ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2 334 (45.9), 487 (46.4), 613 (9.11), 658 nm (7.29). MS (FD), m/z^+ 788 ([MoO(tpp)(NO_3)]$^+$). IR (KBr) ν = 958 (νMo=O); 574 (νMo–O); 1280, 1386, 1476 cm^{-1} (νNO_3). The single crystals of [MoO(tpp)(NO_3)]$\cdot CH_2Cl_2$ for X-ray crystallography were obtained from *n*-pentane–dichloromethane.

Physical Measurements. UV-vis spectra were measured on a Hitachi 808 spectrophotometer or on a Hitachi U-3000 spectrophotometer. IR spectra were recorded as KBr pellets with a Hitachi 270-50 spectrophotometer. ESR spectra were recorded on a JEOL JES-FE1X spectrometer operating at 100 kHz modulation. FAB-MS and FD-MS spectral measurements were carried out using a JEOL JMS-HX 110 spectrometer or a FDKW 2400-R1390 spectrometer.

X-Ray Structural Determinations.[31] The crystals of **1**, **4**, and **5** were obtained, as toluene solvate (**1**$\cdot 2C_6H_5CH_3$), dichloromethane/pentane/water solvate (**4**$\cdot 2CH_2Cl_2 \cdot C_5H_{12} \cdot H_2O$), and dichloromethane solvate (**5**$\cdot CH_2Cl_2$), respectively. The crystals of **1**, **4**, and **5** were sealed in glass capillary tubes and data were collected on a Rigaku AFC-5R (**1**$\cdot 2C_6H_5CH_3$ and **4**$\cdot 2CH_2Cl_2 \cdot C_5H_{12} \cdot H_2O$) or MacScience MXC18 diffractometer (**5**$\cdot CH_2Cl_2$) using graphite-monochromated Mo $K\alpha$ (λ = 0.7107 Å) radiation at 296 K except for **5**$\cdot CH_2Cl_2$ (223 K). The unit cell parameters of **1**$\cdot 2C_6H_5CH_3$ and

Table 3. Crystallographic Data for X-Ray Diffraction Studies

	[MoO(tmp)($C_6H_5SO_3$)]·$2C_6H_5CH_3$ (**1**·$2C_6H_5CH_3$)	[{MoO(tpp)}$_2$(μ-SO_4)]·$2CH_2Cl_2$·C_5H_{12}·H_2O (**4**·$2CH_2Cl_2$·C_5H_{12}·H_2O)	[MoO(tpp)(NO_3)]·CH_2Cl_2 (**5**·CH_2Cl_2)
Formula	$C_{76}H_{73}MoN_4O_4S$	$C_{95}H_{72}Cl_4Mo_2N_8O_6S$	$C_{45}H_{30}Cl_2MoN_5O_4$
Fw	1234.44	1787.42	871.61
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)
a/Å	20.922(5)	13.526(2)	11.345(2)
b/Å	25.832(4)	25.482(6)	13.075(4)
c/Å	12.546(12)	12.905(3)	13.804(4)
α/deg	90	101.26(2)	88.85(2)
β/deg	104.62(3)	97.50(2)	71.99(2)
γ/deg	90	83.15(2)	76.36(2)
V/Å^3	6561(6)	4305(2)	1889.2(9)
Z	4	2	2
T/°C	23	23	−50
λ/Å	0.71069	0.71069	0.71073
d_{calcd}/g cm^{-3}	1.25	1.38	1.53
$2\theta_{\text{max}}$/deg	45	45	45
μ(Mo $K\alpha$)/cm^{-1}	2.75	4.89	5.32
No. of unique rflns	9510	12986	8395
No. obsd rflns	5127, $F_o > 6\sigma(F_o)$	4963, $F_o > 6\sigma(F_o)$	7799, $I > 2\sigma(I)$
$R(F_o)$	0.064	0.082	0.050
$R_w(F_o)$	0.085	0.092	0.060

4·$2CH_2Cl_2$·C_5H_{12}·H_2O were obtained by least-squares refinement of 25 reflections ($25 \leq 2\theta \leq 30°$), while those of **5**·CH_2Cl_2 were obtained by least-squares refinement of 26 reflections ($30 \leq 2\theta \leq 35°$). The intensities of three standard reflections for each compound, monitored every 150 reflections, showed no appreciable decay during the data collection. All data were corrected for Lorentz and polarization effects. No absorption corrections were applied for each compound.

The crystal structure of **1**·$2C_6H_5CH_3$ was solved by standard heavy-atom procedures (UNICS III).[32] The positional and thermal parameters of non-H atoms were refined anisotropically by the block-diagonal-matrix least-squares method. Since the $C_6H_5SO_3^-$ ion was disordered around the coordinated oxygen atom, an occupancy factor of 0.5 was assigned to the atoms in the $C_6H_5SO_2$ moiety. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. No attempt was made to locate H atoms.

The crystal structure of **4**·$2CH_2Cl_2$·C_5H_{12}·H_2O was also solved by standard heavy-atom procedures (UNICS III).[32] The coordinates of the Mo atoms were found from a Patterson map and the remaining non-H atoms were found by successive structure-factor-Fourier calculations. All the non-H atoms were refined anisotropically by the block-diagonal-matrix least-squares method except solvent molecules. Those of solvent molecules were refined isotropically. At the final stage of refinement, carbon atoms in the *n*-pentane molecule (C(P1)–C(P5)) had shifted abnormally. Since the elemental analysis of this compound indicates inclusion of *n*-pentane as a crystallizing solvent, and the difference Fourier calculation after refinement without *n*-pentane molecule shows peaks near the position of C(P1)–C(P5), refinement was terminated after 4-cycles refinement including the C(P1)–C(P5) atoms. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. In the final cycle of the refinement, parameter shifts were less than 0.3σ except for those in the distorted *n*-pentane molecule, for which $\Delta_{\text{max}}/\sigma = 0.95$. No attempt was made to locate H atoms.

The crystal structure of **5**·CH_2Cl_2 was solved by direct methods (SIR92).[33] The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method. The minimized function was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.001|F_o|^2$. H atoms were included at calculated positions with fixed displacement parameters (1.2 times the displacement parameters of the host atom). All calculations were performed using UNICS III[32] for **1**·$2C_6H_5CH_3$ and **4**·$2CH_2Cl_2$·C_5H_{12}·H_2O and CRYSTAN[34] for **5**·CH_2Cl_2. Further crystallographic data are given in Table 3.

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