Solid and Solution State Structures of a Reversible Molecular Oxygen-Carrying Molybdenum Porphyrin Dioxygen Complex

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The molecular structure of a reversible oxygen carrier, $Mo^{VI}O(tmp)(O_2)$ has been characterized by X-ray crystallography. Oxo and dioxygen ligands are actually coordinated with *cis* conformation, which leads to a saddle-like distortion of the porphyrin ring. The result of 2D ROESY shows the distortion of the porphyrin ring is retained in solution.

The uptake of gaseous dioxygen to form dioxygen metal complexes has been extensively investigated in connection with the study of the activation mechanisms of dioxygen, the transport of oxygen in vivo, and the catalytic oxidation of organic substrates.[1] Several such complexes have been structurally characterized by X-ray crystallography and the environment of the coordinating dioxygen ligand has been determined.[2]

We have previously reported that the bulky porphyrin ring complex $Mo^{IV}O(tmp)$ undergoes a reaction with dioxygen to form $Mo^{VI}O(tmp)(O_2)$ **1** at room temperature.[3,4] The complex liberates dioxygen upon irradiation with visible light and is regenerated in the presence of dioxygen when visible light is excluded. This reversible dioxygenation was repeatedly observed both in solution[3] and in the solid state,[5] under photochemical and thermal conditions. The ^1H NMR spectrum of **1** suggested that it had mutually *cis* oxo and dioxygen ligands. We now report a single crystal X-ray diffraction determination of the structure of **1**, along with the assignment of its ^1H and ^{13}C NMR spectra and a study of the structure in solution based on NOE intensities derived from 2D ROESY experiments.[6]

Figure 1 shows the molecular structure of **1** in the crystal state.[7,8] In it, the coordinated oxo and dioxygen ligands are on the same side of porphyrin plane and adopt an eclipsed orientation with respect to one of the *trans* N atoms of the pyrrole rings as shown in Figure 1-a. This structure is identical with that predicted from the ^1H NMR and IR measurements,[3] and is very similar to that of $W^{VI}O(tpp)(O_2)$ which was prepared by the treatment of a tungsten(V) complex with H_2O_2.[9, 10]

The porphyrin core has a pronounced saddle distortion (Figure 1-b) and the central molybdenum atom is displaced by 1.00 Å from the mean plane of the four nitrogen atoms. This displacement is comparable to that in the *cis*-dioxo molybdenum porphyrin complex, $Mo^{VI}(O)_2(ttp)$, in which the molybdenum atom lies above 0.97 Å,[11] and is smaller than that in $W^{VI}O(tpp)(O_2)$ with 1.49 Å.[9]

The O-O distance (1.42(3) Å) is almost the same as that in other peroxo complexes with a $MoO(O_2)$ moiety (1.43 ~ 1.46 Å).[12] The Mo=O distance and mean $Mo-O(O_2)$ distance are 1.697(13) and 1.947(19) Å, respectively. The two Mo-N bonds, eclipsed by the oxo and peroxo ligands, are slightly longer (2.256(7) and 2.320(6) Å) than the other two (2.116(7) and 2.121(7) Å). Similar trends in the metal-nitrogen bonds of porphyrin complexes have been reported in $W^{VI}O(tpp)(O_2)$,[9] in which the coordinated peroxo ligand eclipses the *trans* N atoms of the porphyrin ring.

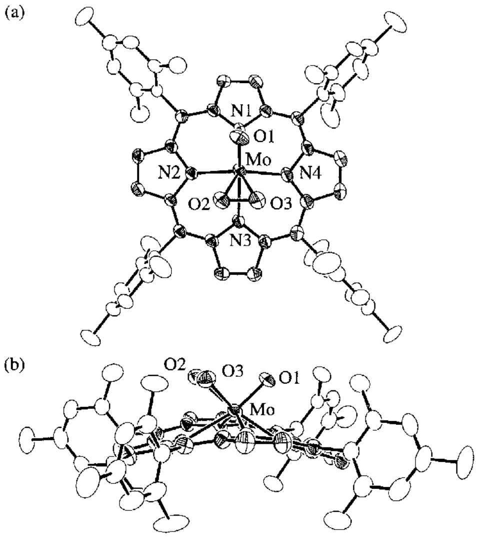

Figure 1. ORTEP drawing of $Mo^{VI}O(tmp)(O_2)$ **1** : top view (a) and side view (b). Selected bond lengths (Å): Mo-O(1) 1.697(13), Mo-O(2) 1.945(18), Mo-O(3) 1.948(19), Mo-N(1) 2.256(7), Mo-N(2) 2.116(7), Mo-N(3) 2.320(6), Mo-N(4) 2.121(7), O(2)-O(3) 1.42(3).

The dihedral angles of **1** between the mean plane of the porphyrin core (24 atoms) and the mesityl rings are smaller on the oxo side (75.4(3) and 65.8(1)°) than on the peroxo side (84.7(3) and 75.9(5)°). This was reflected in the differential NOE intensities observed in the ROESY[13] spectrum and made possible the complete assignment of the ^1H NMR spectrum (Figure 2-b). This assignment confirmed the original conclusion[3] that the C_s symmetry of the tmp ligand of the complex was retained in solution and more detailed consideration of the NOE intensities made it possible to comment on the geometry in solution of the porphyrin ring and the orientation of the mesityl groups. The signals observed in ^{13}C NMR spectrum were also assigned by HSQC[14] and HMBC[15] experiments.

Owing to crystal packing effects, the four mesityl rings in the crystal all have different orientations relative to the (distorted) porphyrin ring. However, in solution there is sufficient librational motion (though not complete rotation) on an NMR time scale for mesityl ring A1 to become equivalent to A2, and B1 to B2, thus giving rise to the effective symmetry plane. On the provisional assumption that rings A1 and A2 are adjacent to the single oxygen atom, then the NOE intensities (from vol-

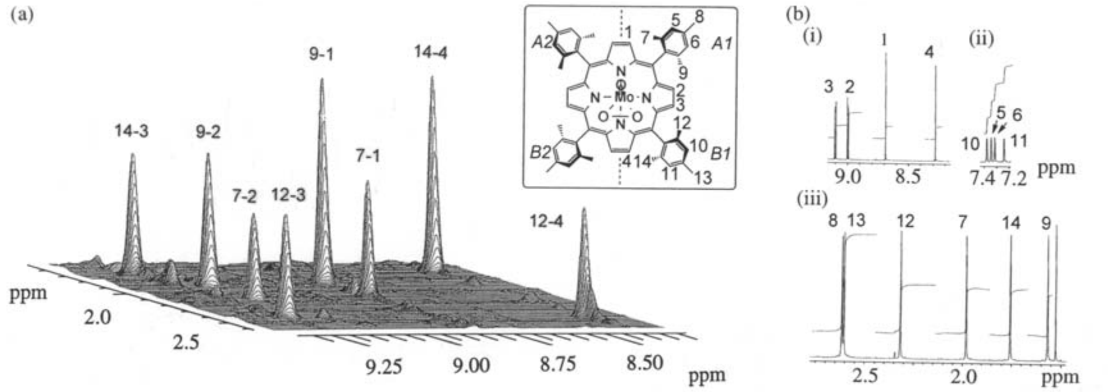

Figure 2. The assignment of ^{1}H NMR spectrum of $Mo^{VI}O(tmp)(O_2)$ **1**. (a): Part of proton ROESY spectrum phased to invert the intensities of all peaks. The eight NOE interactions shown were between the ortho-methyl and the pyrrole protons. (b): ^{1}H NMR spectrum for $Mo^{VI}O(tmp)(O_2)$ **1** in CD_2Cl_2 at 25 °C. Signal showed: β-pyrrole (i), *m*-protons of mesityl groups (ii), and *o*- and *p*-protons of mesityl groups (iii).

ume integrals of the ROESY spectrum, Figure 2-a) between the ortho methyl groups and their adjacent pyrrole protons may be compared with corresponding distances from the solid state structure.

For a planar porphyrin ring with perpendicular mesityl groups, all NOE interactions between the ortho methyl groups and their adjacent pyrrole protons should be equal. In fact this is clearly not so and the observed deviations are consistent with the distorted solid state geometry of the ring being retained in solution. The buckling of the porphyrin ring leads to ortho methyl/pyrrole proton average distances that are shorter (corresponding to larger NOEs) for the underside (i.e. away from the metal) than for the upper side of ring, and this enables us to assign 7 and 12 as "upper" methyl groups. It is also apparent that since NOE interaction 9/1 is not equal to 9/2, and 14/4 is not equal to 14/3, the mesityl rings have average orientations in solution that are not perpendicular to the mean porphyrin plane. To quantify this further would require appropriate r^{-6} averaging calculations and would not be justified by the precision of the measurements.

It also appears that there is a greater difference between the distances above and below the porphyrin ring for the single oxygen end of the molecule and that this is reflected in the experimental NOEs. Thus the ratio (9/1 + 9/2)/(7/1 + 7/2) is 1.59 whereas (14/4 + 14/3)/(12/4 + 12/3) is 1.24 and this leads us tentatively to propose that ring type A is adjacent to the single oxygen.

In summary, in the solid state of $Mo^{VI}O(tmp)(O_2)$ **1** has a structure with mutually *cis* oxo and dioxygen ligands which leads to a saddle-like distortion of the porphyrin ring, one of the nitrogen atoms being eclipsed by the single oxygen atom on a view down the C_s symmetry axis. 2D ROESY NMR experiments show that the puckering of the porphyrin ring is maintained in solution on an NMR relaxation time scale (i.e. of the order of seconds), it being noteworthy that 1D NMR experiments alone cannot provide such information.

References and Notes

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4 Abbreviations; tmp = 5,10,15,20-tetramesitylporphyrinato dianion, tpp = 5,10,15,20-tetraphenylporphyrinato dianion, ttp = 5,10,15,20-tetra(*p*-tolyl)porphyrinato dianion.

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6 Crystallographic data have been deposited at the CCDC, UK. The deposition number is CSD 410412. NMR data were deposited at the office of the Editor of Chemistry Letters.

7 Crystal data for **1** : $C_{56}H_{52}N_4O_3Mo$, Fw = 925.0, monoclinic, space group $P2_1/n$ (No. 14), a = 20.266(4) Å, b = 15.915(4) Å, c = 15.119(3) Å, β = 94.35(2) °, V = 4862(2) Å^3, Z = 4, ρ_{calcd} = 1.263 g/cm^3, Mo Kα (0.71073 Å), μ = 3.07 cm^{-1}, $2\theta_{max}$= 53° (ω-2θ scan), T = 223 K, R = 6.4, R_w = 7.1. 12132 measured reflections, 9577 independent reflections, 6814 observed reflection [I>2.0σ(I)]. The crystal structure was solved by a standard direct method (SIR92). The hydrogen atoms except for the methyl hydrogens of mesityl groups were included at calculated positions with fixed displacement parameters (1.2 times the displacement parameters of the host atom).

8 Oxo and peroxo groups showed 0.24:0.76 disorder. Figure 1 illustrates the structure having high occupancy.

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