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X-Ray Structures of Molybdenum(V) Tetraphenylporphyrins, MoO(tpp)NCS·CH$_2$Cl$_2$ and MoO(tpp)F

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Synopsis. The molecular structures of the title complexes have been determined by a single-crystal X-ray diffraction method. The crystals of MoO(tpp)NCS·CH$_2$Cl$_2$ (tpp= 5,10,15,20-tetraphenylporphyrinato) and MoO(tpp)F are triclinic and tetragonal respectively. An isothiocyanate ion is coordinated to the central molybdenum atom at an angle of 145° with the Mo–N(NCS) bond through the nitrogen atom. In both complexes, the molybdenum atoms are displaced toward oxo ligands from the 4N plane composed of pyrrole nitrogens.

In the substitution reactions of the axial ligand X of Mo^{V}O(tpp)X (X=F, NCS, Cl, Br) with dimethyl sulfoxide (DMSO) in DMSO–CH$_2$Cl$_2$, the values of the formation constants of DMSO complexes are in the order of X=Br>Cl>NCS>F, i.e., the Mo–F bond is stronger than the Mo–NCS bond for the substitution reaction.[1)] The same order was observed for the bathochromic shift of the Soret band in electronic absorption spectrum of a series of these complexes[2)] and also for the shift of the electrochemical half-wave potentials of the central molybdenum atoms.[3)] In addition, the electronic spectral bands of the constrained complexes [Mo^{IV}O(tpp)]$^-$, which are formed by γ-ray irradiation of Mo^{V}O(tpp)X in the glassy matrix of 2-methyltetrahydrofuran at 77 K, shift in the same order as those of Mo^{V}O(tpp)X.[4)] The structure of Mo^{V}O(tpp)X is assumed to be reflected on that of [Mo^{IV}O(tpp)X]$^-$. These facts suggest that the axial ligand X in Mo^{V}O(tpp)X largely affects the reactivity of the molybdenum porphyrins.

In the present paper, we report the structures of MoO(tpp)NCS·CH$_2$Cl$_2$ (**1**) and MoO(tpp)F (**2**) in comparison with other molybdenum porphyrins, focusing on the coordination sphere around the central molybdenum atoms.

Experimental

The complexes **1** and **2** were prepared by the methods reported previously.[2)] The crystals for X-ray data collection were obtained from dichloromethane–hexane solutions in the dark. The electronic spectra of these complexes agreed with those reported previously.[1)]

A Rigaku AFC-6 automated four-circle diffractometer using graphite-monochromatized Mo$K\alpha$ radiation (λ= 0.71073 Å) was used for X-ray measurements. Diffraction data were collected at 298 K using the ω–2θ scan technique for the $2\theta<55°$ range. The crystal of **1** was coated with epoxy-resin avoiding efforescence of the complex during X-ray expepriment, and mounted on the end of a glass capillary. The structures of both complexes were solved by the heavy-atom method. Refinements for **1** and **2** were carried out by the block-diagonal least-squares technique using 7257 reflections and by the full-matrix least-squares technique using 1036 reflections respectively. The final R values $(\Sigma||F_o|-|F_c||/|F_o|)$ were 0.051 and 0.039 for **1** and **2** respectively. The complete F_o–F_c data are deposited as Document No. 8935 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Crystal data of **1**: MoO(C$_{44}$H$_{28}$N$_4$)NCS·CH$_2$Cl$_2$, triclinic, space group P$\bar{1}$, a=13.680(3), b=14.172(2), c=11.213(2) Å, α=106.10(1), β=106.27(2), γ=94.53(2)°, D_{calcd}=1.458 g cm^{-3}, and Z=2. Crystal data of **2**: MoO(C$_{44}$H$_{28}$N$_4$)F, tetragonal, space group I4, a=13.402(3), c=9.730(2) Å, D_{calcd}=1.413 g cm^{-3}, and Z=2.

Results and Discussion

Perspective views of the complexes **1** and **2** are shown in Figs. 1 and 2. The selected bond lengths,

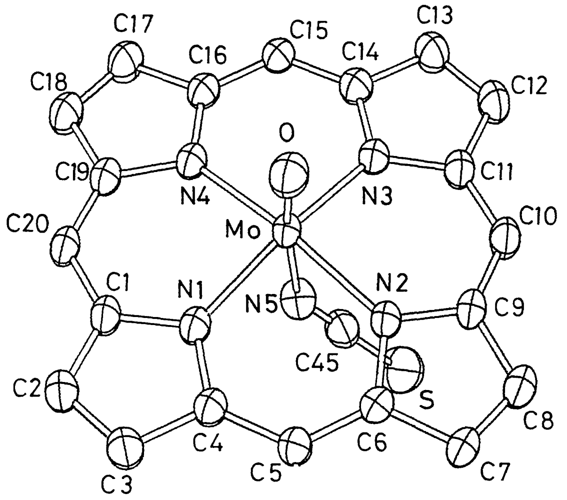

Fig. 1. Perspective drawing of the MoO(tpp)NCS molecule. The phenyl rings of the tetraphenylporphyrinato ligand have been omitted for clarity.

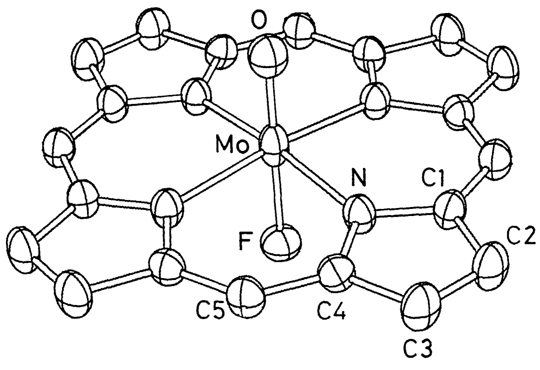

Fig. 2. Perspective drawing of the MoO(tpp)F molecule. The phenyl rings of the tetraphenylporphyrinato ligand have been omitted for clarity.

Table 1. Selective Bond Lengths and Bond Angles with Estimated Standard Deviations in Parentheses

Bond length/Å		Bond/torsion angle/°	
$MoO(tpp)NCS \cdot CH_2Cl_2$			
Mo–O	1.673(3)	O–Mo–N1	99.1(1)
Mo–N1	2.079(2)	O–Mo–N2	96.1(2)
Mo–N2	2.094(3)	O–Mo–N3	97.6(1)
Mo–N3	2.086(3)	O–Mo–N4	98.2(2)
Mo–N4	2.085(3)	N1–Mo–N5	84.5(1)
Mo–N5	2.257(4)	N2–Mo–N5	78.9(1)
N5–C45	1.160(6)	N3–Mo–N5	78.8(1)
C45–S	1.612(5)	N4–Mo–N5	86.8(1)
Δ[a]	0.282(4)	Mo–N5–C45	144.7(4)
		N5–C45–S	179.0(4)
		N2–Mo–N5–C45	−36.1(5)
		N3–Mo–N5–C45	55.8(5)
MoO(tpp)F			
Mo–O	1.677(12)	O–Mo–N	94.3(2)
Mo–N	2.089(3)		
Mo–F	1.967(9)		
Δ[a]	0.155(9)		

a) Displacement distance of molybdenum atom from the 4N plane formed by pyrrole nitrogens.

bond angles, and torsion angles are shown in Table 1. In the complex **1**, the isothiocyanate ion is in a staggered conformation with respect to the pyrrole nitrogens and is coordinated on the central molybdenum atom through the nitrogen atom, which justifies the assumption obtained by visible absorption spectral measurements.[2] The bond length of Mo–N5(NCS) (2.257 Å) belongs to the category of relatively long length among the bond lengths (2,05—2,27 Å) observed for non-porphyrin molybdenum isothiocyanate complexes, and the angle Mo–N5–C45(NCS) (144.7°) is a little smaller than the related complexes (160—180°).[5] The molybdenum atom lies at 0.282 Å from the 4N plane formed by the pyrrole nitrogens toward the O atom, which is reflected on the large angles of O–Mo–N(1—4) (96.1—99.1°) compared to those of N(1—4)–Mo–N5(NCS) (78.8—86.8°). The Mo–O bond length (1.673 Å) is longer by 0.017 Å than the Mo–O bond length (1.656 Å) of MoO(ttp)[6] (ttp=5,10,15,20-tetra-*p*-tolylporphyrinato) having no axial ligation of X and is shorter than the terminal Mo–O bond length (1.707 Å) in $[MoO(tpp)]_2O$.[7] In contrast with the structure of **1**, **2** has a simple C_4 symmetry. The Mo–O bond length is 1.677 Å. The molybdenum atom lies at 0.155 Å from the 4N plane and the O–Mo–N bond angle is 94.3°. The Mo–F bond length (1.967 Å) is not so different from the sum of covalent radii (1.94 Å) of Mo and F atoms and is compared well with the bond length (1.96—1.77 Å) of non-porphyrin fluoromolybdenum complexes.[8] In MoO(tpp)Cl,[9] the bond lengths, Mo–O (1.714 Å) and Mo–N (2.118 Å), and the displacement distance of molybdenum atom from the 4N plane (0.390 Å) are all larger than those in **1** and **2**. The bond length of Mo–Cl (2.494 Å), which is longer than the sum of the covalent radii (2.29 Å) of Mo and Cl atoms, suggests a large amount of ionic character for the bond.[9] Although we can not refer directly to reactivity of these three complexes, **1**, **2**, and MoO(tpp)Cl in solutions on the basis of these crystal data, the Mo–Cl bond is expected to be weak for substitution. In practice, the axial ligand Cl^- of MoO(tpp)Cl is more easily substituted by DMSO cmpared with **1** and **2**.[1] The displacement of the central molybdenum atoms is in the order of MoO(tpp)Cl>**1**>**2** that is parallel to the order of easiness of the substitution reactions: the stronger the Mo–X bond is, the smaller the displacement. The absence of axial ligand at the trans position of the oxo ligand causes large displacement of the molybdenum atom toward the oxo ligand from the 4N plane as observed in the complexes of MoO(ttp) (0.6389 Å)[6] and $Mo(O)_2(ttp)$ (0.972 Å).[10]

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