Sulfur-bridged incomplete cubane-type molybdenum clusters have attracted much attention due to their reactivity toward metals, metal ions or organometallic compounds to produce a mixed-metal cluster having a cubane-type Mo₃M₄ core. The title compound, [{Mo₃S₄(Tpms)₂}₂(m-O)(m-Cl)₂]·5CH₂Cl₂, was obtained by the reaction of [Mo₃S₄(H₂O)₉]⁴⁺ with LiTpms. The starting complex and LiTpms were prepared according to literature procedures. The title compound was prepared by the following method: A solution of [Mo₃S₄(H₂O)₉]⁴⁺ (0.1 M per trimer) in 2 M HCl (5 mL, 0.5 mmol) was evaporated to dryness under reduced pressure. The green residue was dissolved in methanol (30 mL) to generate a green solution. To this green solution was added a methanol solution (10 mL) containing LiTpms (585 mg, 1.95 mmol), and the resulting solution was stirred overnight. The green powder and LiCl precipitated together during stirring. The precipitates were collected by filtration and washed with water to remove the LiCl. The green powder was recrystallized from a saturated CH₂Cl₂ solution at room temperature. Green single crystals for X-ray analysis were obtained after leaving the solution standing for two days.

Anal. Calcd for C₄₁H₃₈Cl₄Mo₆N₂₄O₁₃S₁₂: C, 22.62; H, 1.76; N, 15.44. Found: C, 22.31; H, 1.88; N, 15.40.

The structure was solved using the SHELXTL program package software. All of the atoms were anisotropically refined. All hydrogen atoms were included in the refinement at calculated positions, riding on their carrier atoms (C–H 0.95 Å). Isotropic thermal parameters of hydrogen atoms were constrained to 1.2 Ueq, to which they were attached.

The structure compound, [{Mo₃S₄(Tpms)₂}₂(m-O)(μ-Cl)₂]·5CH₂Cl₂ (Tpms = tris(pyrazolyl)methanesulfonate), crystallized in the monoclinic space group C2/c with the following unit-cell parameters: a = 24.509(7)Å, b = 29.273(6)Å, c = 16.490(5)Å, β = 132.942(3)°, V = 8661(4)Å³ and Z = 4. The crystal structure was solved by direct methods, and refined by full-matrix least-squares procedures to a final R-value of 0.0798 for 7989 observed reflections. A Tpms ligand coordinated to the molybdenum atom through the two nitrogen atoms in two pyrazole rings and one oxygen atom in a sulfonato group. Another Tpms ligand coordinated to the molybdenum atom through three nitrogen atoms in three pyrazolyl rings. The remaining molybdenum atom was bridged to an adjacent molybdenum atom in another Mo₃S₄ core by two chloride anions and one oxygen atom.

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refinement details and structural parameters are summarized in Table 1. The chemical structure is shown in Fig. 1, and an ORTEP drawing of the complex cation is shown in Fig. 2.

Crystal structure analysis has revealed that the two incomplete cubane-type Mo₃S₄ cores are bridged by two chloride ions and one oxygen atom. Furthermore, this compound shows two different coordination modes of the Tpms ligand. The first motif is N,N,O-coordinating form A; the second one is N,N,N-coordinating form B. The Tpms ligand is coordinated to the molybdenum atom through the two nitrogen atoms in two pyrazole rings and one oxygen atom in a sulfonato group in form A, and three nitrogen atoms in three pyrazole rings in form B.

The selected bond distances are listed in Table 2. The different coordination modes of molybdenum atoms slightly influence the Mo-Mo bond distances. The Mo1-Mo3 distance is slightly longer than those of the others. Although there are little differences in the Mo-S bond distances (2.244(3) - 2.379(3)Å in [(Mo₃S₄(Tpms)₂)₂(µ-O)(µ-Cl)]·5CH₂Cl₂), they are still comparable to those observed in the clusters [Mo₃S₄(H₂O)₁₀](pts)₄·9H₂O⁴, [Mo₃S₄(Tp)₃]Cl·4H₂O⁵ (Tp = hydrotris pyrazolyl borate) and [(Mo₃S₄(Tp)₂)₂(µ-O)(µ-C₃H₃N₂)]·2THF⁶.

Acknowledgments

The authors acknowledge support by the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2009-2013.

References