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Synthesis and X-Ray Crystal Structure of a Novel Malonato Bridged Tetrameric Molybdenum(V) Complex, $K_6[\{Mo_2O_4(mal)_2\}_2(mal)]\cdot 4H_2O$

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Many molybdenum(V) compounds containing Mo_2O_4 core, which is dominant in Mo(V) chemistry, have been prepared in aqueous solution [1]. The oxalato complex is the only example so far prepared to contain a dicarboxylic acid as a ligand [2]. We will report here a synthesis and structural study on a novel malonato complex and compare its structure with that of the oxalato complex [3].

The potassium salt of the complex was prepared by the following procedure: to the malonic acid (H_2-mal; 2.1 g or 0.02 mol) in 50 ml of water, $[pyH]_2[MoOCl_5]$ (4.5 g or 0.01 mol) was added and the solution was heated for *ca.* 40 min at 80–90 °C. After the solution had been cooled to room temperature, its pH was adjusted to *ca.* 4.7 with dilute KOH solution. Potassium chloride (1.0 g) was added with stirring and then the solution was made turbid by the addition of ethanol. Brick red crystals were obtained by filtration after standing for several days in a refrigerator and washed successively with ethanol and diethyl ether; yield 1.8 g.

The compound crystallizes in the monoclinic system, space group $P2_1$ with cell dimensions a = 12.832(3), b = 20.848(9), c = 7.471(1) Å, β = 94.96(1)° and $Z = 2$. Intensity data were collected on a Phillips PW1100 four-circle diffractometer using graphite monochromatized Mo-$K\alpha$ radiation (λ = 0.7107 Å) with ω-scan technique. The structure was determined by the Patterson and Fourier procedures and refined by block-diagonal least-squares methods to a final R value of 0.043 for 4006 ($F_o^2 > 3\sigma(F_o^2)$) reflections collected in the $2\theta \leqslant 55°$ range. All but hydrogen atoms were refined anisotropically.

The overall symmetry of the complex ion is close to C_{2v}; there is an approximate two-fold rotation axis through the C2 atom of the malonato bridge as shown in Fig. 1, and the coordination scheme is totally different from the oxalato complex, $Ba[Mo_2O_4(ox)_2(H_2O)_2]\cdot 3H_2O$ [3], where the ligating oxygen atoms in the oxalato ligand are in *cis* and *trans* positions to the terminal oxygen. The malonato complex anion contains two types of malonato ligands; one is a bidentate chelate ligand which coordinates to one Mo(V) atom to form a six-membered ring and has a boat conformation [4], the other is a quadridentate ligand to form a bridge between two $Mo_2O_4(mal)_2$ moieties. No report, to our knowledge, has so far appeared on the quadridentate malonato complexes.

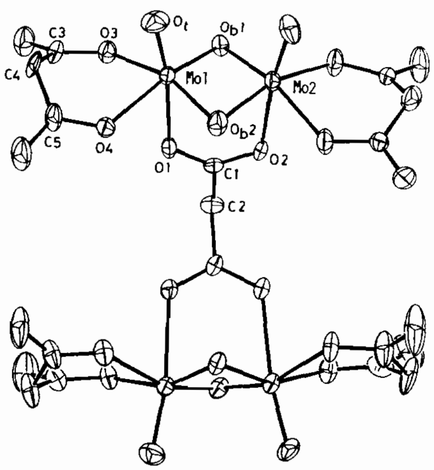

Fig. 1. Structure of the $[\{Mo_2O_4(mal)_2\}_2(mal)]^{6-}$ anion.

The distances** Mo1–Mo2 (2.555 Å), Mo1–Ot (1.684 Å), and the displacement (0.37 Å) of Mo1 towards Ot from the mean plane defined by four oxygens (Ob1, Ob2, O3, and O4) are in good agreement with those of Mo_2O_4 cores previously reported [1, 5]. The C–C–C angle (115°) of the bridging malonato anion is essentially the same as the mean angle (116°) of the four non-bridging malonato C–C–C angles. The distance Mo1–O1 (2.321 Å) is evidently longer than that of Mo1–O3 (2.081 Å) indicating the *trans* influence of Ot. The oxalato complex has been known to show no *trans* influence due to the terminal oxo ligand [3], and it is also the case with the di-μ-sulfido oxalato complex, $Cs_2[Mo_2O_2S_2(ox)_2(H_2O)_2]\cdot 2H_2O$ [6]; the coordination scheme is, however, different between the malonato and oxalato complexes and direct comparison should not be made straightforwardly. The angle Ot–Mo1–O1 (θ_1 = 171°) and the dihedral angle between the Mo1, Ob1, and Ob2 plane and the Mo2,

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**Average value of two to eight distances.

Ob1, and Ob2 one (θ_2 = 161°) are considerably larger than those of similar types of complexes having Mo_2O_4 core[†]. These can be attributed to the short O1–O2 distance (2.230 Å) caused by the coordination of the bridging malonato anion as a quadridentate ligand. The UV and visible spectra show a peak and a shoulder at 315 (ϵ = 11200) and 420 nm (ϵ = 720), respectively. The deformation of Mo_2O_4 core by the bridging malonato anion may be responsible for the red shift of the CT band around 300 nm[††].

[†] E.g. for $[Mo_2O_4(ox)_2(H_2O)_2]^{2-}$, θ_1 = 159° and θ_2 = 150.6° calculated using the atomic parameters by Cotton and Morehouse [3]; for $[Mo_2O_4(cys)_2]^{2-}$, θ_1 = 162.6° and θ_2 = 151°.

[††] The oxalato complex has an absorption peak and a shoulder at 305 (ϵ = 7040) and 384 nm (ϵ = 340), respectively.

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