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Conversion of Malonate and Malate to Oxalate in Aqueous Peroxo Molybdate(VI) Solutions. Synthesis and Structure of Potassium Oxodiperoxooxalatomolybdate(VI)

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A variety of peroxoheteroligand complexes of the early transition metals in their high oxidation states is known [1, 2, 3]. Peroxo compounds represent an important class of reactive intermediates in catalytic oxidation [4, 5, 6], and are therefore of importance in biological processes involving oxidation, or conversion of dioxygen species. Molybdenum and vanadium, the two 'trace elements' essential for living matter [7] are especially interesting in this respect [3, 8, 9]. We have recently reported the synthesis and properties of a number of peroxoheteroligand molybdates(VI) and vanadates(V) [10], and now report the discovery of a catalytic conversion of two dicarboxylato ions used as heteroligands in aqueous peroxomolybdate(VI) systems.

Pale yellow crystals of the potassium oxodiperoxooxalatomolybdate(VI), $K_2[MoO(O_2)_2(C_2O_4)]$, were obtained from the aqueous solutions in which malonic acid was present and expected to coordinate to molybdenum. Following the usual procedure to prepare a peroxoheteroligand metal complex, an equimolar amount of malonic acid was added to the colorless solution of MoO_3, dissolved in potassium hydroxide, to which an excess of hydrogen peroxide was added. After standing at room temperature (or treated with ethanol) a crystalline precipitate was obtained at pH about 3 (approx. yield 30%). Repeated preparations under varied experimental conditions (temperature and concentration) changed only the time of crystallization and the yield, but not the product. Analysis (C, K, Mo, O_2^{2-} and $C_2O_4^{2-}$) of the crystals agreed well with the formula $K_2[MoO(O_2)_2(C_2O_4)]$, and the determination of peroxides in the presence of oxalates and molybdenum was possible by potentiometric titration with Ce(IV), where peroxides oxidize first, followed by the oxidation of oxalates at an about 250 mV higher potential. The compound was further characterized by infrared spectra and X-ray structure analysis.

The structure of $K_2[MoO(O_2)_2(C_2O_4)]$, prepared differently, was reported in 1970 [11]. Crystal data which we have obtained agree well with the previous data regarding the unit cell, the space group, and the arrangement of the complex ion. However, since the previously reported structure was refined to R = 11.2%, the bond lengths were determined with a standard deviation of 0.011–0.025 Å. A greater accuracy is now required in order to assess more accurately the influence of the metal ion and ligand fields on the symmetry and the reactivity of coordinated peroxo group. We therefore report here our results of the structural analysis of $K_2[MoO(O_2)_2(C_2O_4)]$. The stereoview of the complex anion is shown in Fig. 1, and the ionic packing in Fig. 2. Principal bond lengths and bond angles are given in Tables I and II. Cell dimensions and space group were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. $C_2O_9K_2Mo$ crystals are monoclinic, belonging to the space group $P2_1/n$, with a = 6.912(2) Å, b = 8.852(3) Å, c = 13.747(4) Å, β = 92.51(2)°, and Z = 4. Absorption coefficient = 25.3. Of the total 2968 independent intensities, 2068 (within 3σ) were used. A three-dimensional Patterson synthesis was used to determine the heavy atom positions, which phased the data sufficiently well to permit location of the remaining atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described [12, 13]. Anisotropic temperature factors were introduced. The model converged with R = 3.4%, and R_w = 5.1%. A final Fourier difference map was featureless. A listing of the observed and calculated structure factors, the positional and the thermal parameters, as well as selected least-square planes through groups of atoms, are available upon request from the authors.

TABLE I. Interatomic Distances (Å) for $K_2[MoO(O_2)_2(C_2O_4)]$.[a]

Mo–O	1.676(1)	O(p1)–O(p2)	1.480(2)
Mo–O(p1)	1.941(1)	O(p3)–O(p4)	1.466(2)
Mo–O(p2)	1.958(1)	O(1)–C(1)	1.277(1)
Mo–O(p3)	1.938(1)	O(2)–C(1)	1.210(2)
Mo–O(p4)	1.961(1)	O(3)–C(2)	1.301(2)
Mo–O(1)	2.269(1)	O(4)–C(2)	1.217(2)
Mo–O(3)	2.051(1)	C(1)–C(2)	1.557(2)

[a] The digits in parenthesis in the Tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations.

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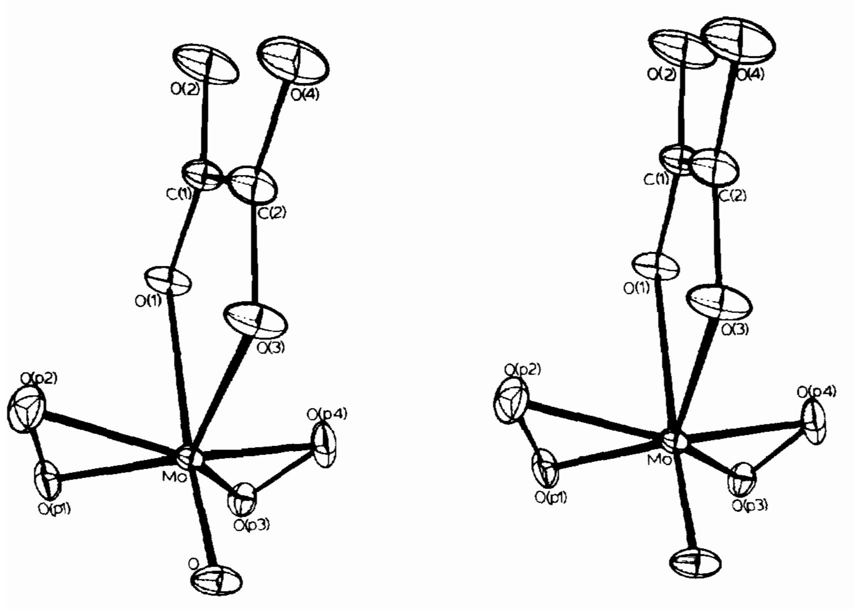

Fig. 1. Stereoview of the $[MoO(O_2)_2(C_2O_4)]^{2-}$ anion. Molybdenum is in a distorted pentagonal bipyramid, with the oxo group and a carboxylato oxygen at the apical positions. The equatorial plane consists of the other carboxylato oxygen and two peroxo groups, with the (O–O) bond lengths (1.480(2); 1.466(2)) definitely longer than in some complex peroxo vanadates(V) [15].

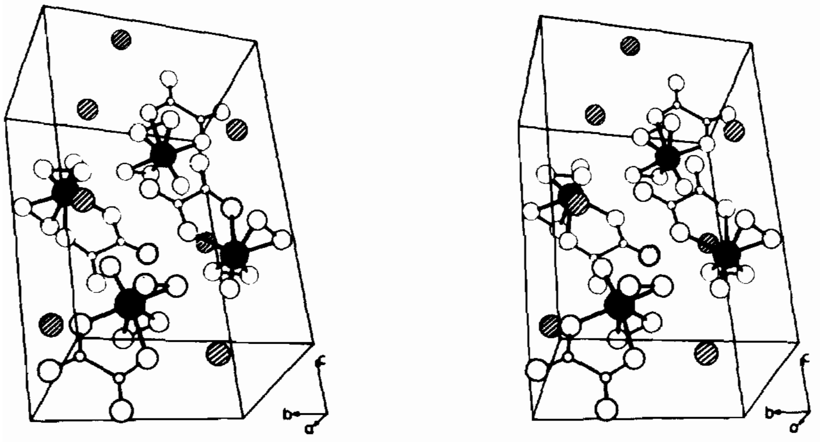

Fig. 2. Ionic packing of $K_2[MoO(O_2)_2(C_2O_4)]$ in the unit cell. The structure consists of potassium cations and complex anions.

The infrared spectrum of $K_2[MoO(O_2)_2(C_2O_4)]$ proved to be very useful in identifying products of various experiments, and since it was not reported previously, the most important bands are described here. The very strong band, resolved as a quartet at 1740, 1700, 1680 and 1660 cm^{-1} is assigned to CO stretchings. A very strong band at 970 cm^{-1} represents the MoO stretch, and a complex band at 865 cm^{-1} the (O–O) stretchings, occurring at a frequency expected in peroxoheteroligand molybdates(VI) [10, 14].

The mechanism of the malonate → oxalate catalytic conversion is at this point unknown. A few preliminary experiments which we have done may contribute to elucidate it. We tested the succinic acid, the next higher homologue of the malonic acid. This acid does not change in peroxomolybdate(VI) solutions. The malic acid (α-hydroxysuccinic acid), however, behaves very much like the malonic acid, and we have separated $K_2[MoO(O_2)_2(C_2O_4)]$ from the solutions (prepared as described above) containing the malic instead of the malonic acid. This behavior indicates that the chelation of the dicarboxylic acid to a peroxo Mo(VI) species is necessary for the conversion, since both malonate and malate are capable of forming six- or five-membered rings, and only an unfavorable seven-membered ring would be possible with succinic acid. Although the peroxomalonato and peroxomalato molybdates(VI) are not isolated from the solutions, they must exist as intermediates, which

TABLE II. Bond Angles (deg) for $K_2[MoO(O_2)_2(C_2O_4)]$.

O–Mo–O(p1)	105.21(5)	O(p3)–Mo–O(3)	129.86(5)
O–Mo–O(p2)	101.92(6)	O(p4)–Mo–O(1)	78.80(5)
O–Mo–O(p3)	103.13(5)	O(p4)–Mo–O(3)	86.90(5)
O–Mo–O(p4)	100.46(6)	O(1)–Mo–O(3)	74.74(4)
O–Mo–O(1)	169.41(4)	Mo–O(p1)–O(p2)	68.30(6)
O–Mo–O(3)	94.68(5)	Mo–O(p2)–O(p1)	67.08(6)
O(p1)–Mo–O(p2)	44.62(5)	Mo–O(p3)–O(p4)	68.74(6)
O(p1)–Mo–O(p3)	88.44(4)	Mo–O(p4)–O(p3)	67.09(6)
O(p1)–Mo–O(p4)	130.33(5)	Mo–O(1)–C(1)	115.09(8)
O(p1)–Mo–O(1)	82.75(4)	Mo–O(3)–C(2)	120.95(9)
O(p1)–Mo–O(3)	131.41(5)	O(1)–C(1)–O(2)	126.89(12)
O(p2)–Mo–O(p3)	131.24(5)	O(1)–C(1)–C(2)	113.84(10)
O(p2)–Mo–O(p4)	157.43(5)	O(2)–C(1)–C(2)	119.27(12)
O(p2)–Mo–O(1)	78.67(5)	O(3)–C(2)–O(4)	123.61(12)
O(p2)–Mo–O(3)	88.43(5)	O(3)–C(2)–C(1)	115.07(11)
O(p3)–Mo–O(p4)	44.17(5)	O(4)–C(2)–C(1)	121.32(12)
O(p3)–Mo–O(1)	83.79(4)		

then convert to oxalates. The stability of the complex anion and the lattice energy of $K_2[MoO(O_2)_2(C_2O_4)]$ enable a simple separation of one of the products of this reaction, the oxalate. The mechanism of this process involves probably several intermediates and rearrangements of a complex oxidative decarboxylation. The use of isotopically labelled reagents and characterization of other reaction products are needed to fully understand it.

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