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# Short Communications

## Crystal and Molecular Structure of Tetra-ammonium *aa'*-μ-Oxobis-{[*gied'*-μ$_3$-(*S*)-malato-*O*$^1$,*O*$^2$,*O*$^4$,*O*$^{4'}$]-di-μ-oxobis[dioxomolybdate(VI)]} Monohydrate. $^{13}$C NMR Studies

JAN-ERIC BERG,[a] SVANTE BRANDÄNGE,[b] LARS LINDBLOM [b] and PER-ERIK WERNER [a]

[a] Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden and [b] Department of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

Molybdate(VI) complexes of optically active α-hydroxy acids were studied polarimetrically as early as at the end of the nineteenth century.[1] More recently, the use of such complexes in determinations of absolute configurations of α-hydroxy acids by CD has been described [2] and the crystal and molecular structure of $(NH_4)_4[(MoO_2)_4O_3(C_4H_3O_5)_2].6H_2O$, obtained from malic acid and ammonium molybdate(VI), has been determined.[3] This compound, known as ammonium dimolybdomalate, was crystallized from water, but if aqueous ethanol is used instead, a compound corresponding to the formula $(NH_4)_4[(MoO_2)_4O_3(C_4H_3O_5)_2].H_2O$ (*1*) is obtained. The crystal structure of *1* is reported here and also the results of $^{13}$C NMR studies which indicate that for the complex in aqueous solution both carboxyl groups of the malic acid are bonded to molybdenum.

*X-Ray diffraction studies.* No crystals of *1* suitable for single crystal analysis were obtained, but a powder photograph was taken with a focusing Guinier-Hägg camera. Strictly monochromatic Cu$K\alpha_1$ radiation ($\lambda = 1.54051$ Å) was used and potassium chloride was added as an internal standard ($a = 6.2930$ Å at 25 °C). The powder photograph was measured by an automatic film scanner system as described by Malmros and Werner [4] and 120 integrated intensities were obtained corrected for polarisation, Lorentz and geometrical factors. A monoclinic cell (space group *C*2, $a = 14.572(2)$ Å, $b = 10.114(2)$ Å, $c = 11.461(2)$ Å, $\beta = 121.45(1)°$, cell volume 1441.0 Å$^3$, $Z = 2$, $D_x = 2.10$ g/cm$^3$) was found by a trial-and-error indexing programme (TREOR).[5,6]

A three-dimensional Patterson function was calculated from the 120 integrated intensities. The two Mo-positions in the asymmetric unit were derived from the Patterson function using space group *C*2. A least squares refinement of the Mo-positions ended with an *R*-value of 0.30. Since no model for the oxygen coordination around the molybdenum atoms could be derived from the integrated intensities, a modified Rietveld profile analysis refinement procedure was applied. The original refinement programme [7] which was written for neutron diffraction data has been rewritten by Malmros and Thomas [8] for X-ray Guinier powder data. The use of profile intensities instead of the integrated intensities makes it possible to take full account of the overlaps. An important advantage of using a focusing film camera instead of a powder diffractometer for the determination of diffraction intensities is the high resolution of the diffraction data. The simultaneous collection of intensities from all diffraction angles during the time of exposure is of course of special importance when unstable compounds are dealt with, as in the present structure determination. On the other hand, no accurate atomic positions could be refined from this powder photograph. However, from successive profile refinements and Fourier calculations, a low resolution structure showing the main features of the structure could be obtained. A structure refinement where the positions of 2 Mo, 12 O and 2 N atoms were refined ended with a reliability factor

$$\sum_{hkl} |\sqrt{I}_{obs} - \sqrt{I}_{calc}| / \sum_{hkl} \sqrt{I}_{obs} = 0.11$$

Four carbon atoms were kept in fixed positions and the total number of parameters refined was 51. The refinement, which included 505 reflections, did not completely converge and therefore no accurate positional coordinates with standard deviations can be given. The structure of the anion (Fig. 1) is indistinguishable from that in ammonium dimolybdomalate.[3] The main difference between the two structures is found in the packing of the ions in the unit cells. This is obviously an effect of the different contents of crystal water in the two compounds. Full crystallographic details will be published elsewhere.

*$^{13}$C NMR measurements.* The CD properties of acidified aqueous solutions containing (−)-malic

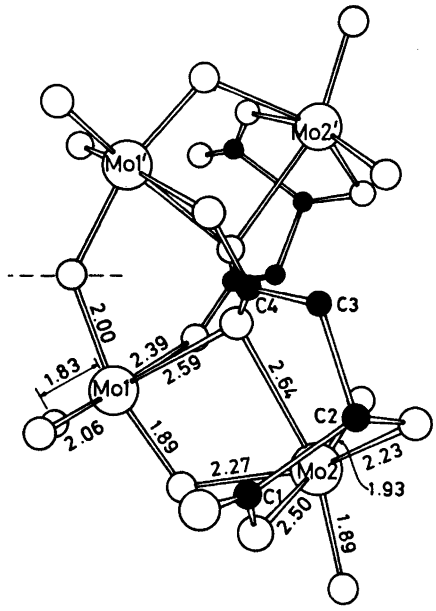


*Fig. 1.* View of the anion $[(MoO_2)_4O_3(C_4H_3O_5)_2]^{4-}$ in the crystal structure of the title compound. E.s.d. in the bond lengths given in the figure are approximately 0.15 Å. The twofold axis is indicated by a dashed line.

acid and molybdate(VI) suggest that both carboxyl groups in the organic acid are involved in the bonding to molybdenum.[2] The following $^{13}C$ NMR results are in agreement with such bonding. The spectrum of a solution of malic acid and sodium molybdate (2 equiv.) in $D_2O$ [pD = pH (meter reading) + 0.40 [9] = 3.9, dioxane as internal standard, $\delta_C = 67.4$ ppm] does not indicate the presence of more than one complex; four signals were found at $\delta$ 184.3, 180.1, 80.3, and 40.4 ppm. Down-field shifts are obtained in going from malic acid to its molybdate complex: C-1 +5.9 ppm; C-4 +4.2 ppm (alternatively: C-1 +1.7 ppm; C-4 +8.4 ppm); C-2 +12.1 ppm; C-3 +0.6 ppm. The fact that the down-field shift of C-4 is larger than that of C-3 indicates that both carboxyl groups of malic acid are bonded to molybdenum. For acetic acid present in the solutions the following values were observed: C-1 +0.0 ppm; C-2 +0.2 ppm.

When citric acid was substituted for malic acid three main signals were obtained in the carboxyl region of a spectrum run at 5 °C ($\delta$ 184.4, 179.5, and 174.8 ppm respectively). This indicates that one of the two $\beta$-carboxyl groups bonds to molybdenum whereas the other does not.

*Preparation of the complex.* Solutions of (−)-malic acid (4.5 g) in water (15 ml) and ammonium heptamolybdate (4.0 g) in water (25 ml) were prepared with some warming. The solutions were filtered and then combined. Boiling ethanol (185 ml) was added under warming to the aqueous solution. On cooling crystals deposited (2.5 g, 48 %). Found: C 10.65; H 2.53; Mo 42.04; N 6.32. Calc. for $(NH_4)_4[(MoO_2)_4O_3(C_4H_3O_5)_2].H_2O$: C 10.53; H 2.65; Mo 42.08; N 6.14. $[\alpha]_{546}^{22}$ +245° (*c* 0.65, water). Lit.[10] value for ammonium dimolybdomalate: $[\alpha]_{546}$ +239° (*c* 2.8, water).

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