

# Ammonium $\mu$ -Formato-di- $\mu$ -oxo-bis[bis(formato)oxomolybdate(V)]. Chemical Properties, Structure and Electronic Spectrum

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We have previously reported the synthesis<sup>1</sup> and crystal structure<sup>2</sup> of sodium hexakis(formato)molybdate(III), which was used to prepare the alum,  $\text{Cs}[\text{Mo}(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .<sup>1,3</sup> The possibility of being able to prepare aqua complexes by acid hydrolysis of formato complexes and the wish to characterize the atmospheric oxidation product of  $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$  led us to undertake an investigation of formato complexes of molybdenum(V). By addition of ethanol to a solution of  $(\text{NH}_4)_2[\text{MoOCl}_5]$  in ammonium formate the compound  $(\text{NH}_4)_3[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]$  (**1**) precipitated as large red crystals. The preparation of this compound had only been reported in the early literature.<sup>4,5</sup> While our work was in progress the X-ray crystal structure of  $(\text{NH}_4)_3[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]$  was reported.<sup>6</sup> The formato complex has the expected property of being converted into the aqua ion  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  of the  $[\text{Mo}_2\text{O}_4]^{2+}$  core when treated with a strong non-complexing acid. Provided that the presence of formic acid is acceptable, purification of the solution is not necessary. The usual methods<sup>7,8</sup> for the preparation of  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  require the removal of chloride by cation exchange.

## Experimental

**Preparation of (1).**  $(\text{NH}_4)_2[\text{MoOCl}_5]$ <sup>9</sup> (3.25 g; 10 mmol) was dissolved in 20 ml 5 M ammonium formate solution which was 5 M with respect to formic acid. The red solution which was thereby obtained was quickly mixed with 20 ml ethanol and set aside for precipitation. Usually after 1 day large red crystals of **1** appeared. The product was washed with 96% ethanol, in which it is insoluble. Yield: 2.25 g (85%). The compound could be purified by reprecipitation: 2.25 g **1** were dissolved in 20 ml 5 M formic acid. In this solution 3.15 g ammonium formate were dissolved and 20 ml ethanol were added. Analyses for Mo, C, H and N were in accordance, within  $\pm 0.4\%$  units, with the formula given. The presence of dioxygen appeared not to reduce the quality of the product.

**Crystal structure determination.** Data were collected on a Huber four-circle diffractometer from a crystal coated with

a butyl methacrylate resin to prevent oxidation. The structure was determined from Patterson and Fourier syntheses, and refined by the method of least squares (on  $F$ ), with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for the formate hydrogen atoms. The ammonium ions were assumed to be rotating freely. Crystal data, details of data collection and results of

Table 1. Crystal data and details of data collection and structure refinement.

Formula weight/g mol <sup>-1</sup>	535.08
Space group	<i>Pnma</i>
Cell parameters (294 K):	
<i>a</i> /Å	7.572(3)
<i>b</i> /Å	17.958(4)
<i>c</i> /Å	11.816(3)
<i>V</i> /Å <sup>3</sup>	1606.7(8)
No. of reflexions centred	35
2 $\theta$ range /°	11–35
Calculated density (294 K)/g cm <sup>-3</sup>	2.212
Molecules per cell	4
Crystal size/mm <sup>3</sup>	0.488 × 0.348 × 0.140
Radiation (Mo <i>K</i> $\alpha$ )	0.71073
Filter	Nb
Linear absorption coefficient $\mu/\text{cm}^{-1}$	15.98
Range of transmission factors	0.659–0.889
Scan type	$\omega$ -2 $\theta$
$\omega$ -Scan width $\Delta\theta$ /°	0.8 + 0.346 tan $\theta$
No. of steps	50
Time per step/s	1
$\theta$ limits/°	1–30
Octants collected	$-h \pm k + l$
Standard reflexions	0 0 4, 0 8 0
Fall-off in intensity/%	1.3
No. of unique data	2407
No. of data with $I/\sigma(I) > 3.0$	1444
$R_{\text{int}}$	0.060
No. of variables	127
Weights $w^{-1} = [\sigma_{\text{cs}}(F^2) + 1.03 \times F^2]^{-1} -  F $ :	
$R = \Sigma( F_o  -  F_c )/\Sigma F_o $	0.029
$Rw = \Sigma w( F_o  -  F_c )^2/\Sigma w F_o ^2$	0.033
$S$ (goodness of fit)	1.09
$\Delta/\sigma_{\text{max}}$	0.19
$\Delta\rho_{\text{max}}/e \text{ \AA}^{-3}$	0.6(1)

the refinement are summarized in Table 1. Tables of coordinates and anisotropic thermal parameters and lists of observed and calculated structure factors are available from the authors on request.

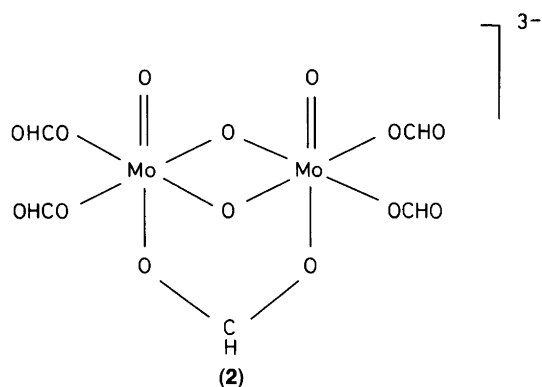
A half-normal probability plot<sup>10</sup> comparing the refined coordinates of this structure determination with that of Kamenar *et al.*<sup>6</sup> gave a straight line ( $r = 0.993$  for 38 variables) with gradient 1.419(28) cutting the  $y$ -axis at  $-0.002(28)$ , indicating that the two determinations are essentially similar.

**Absorption spectra.** UV-VIS spectra were measured in a protective atmosphere of dinitrogen on a Cary 11 spectrophotometer.

## Results and discussion

**Synthetic aspects.** Barbieri<sup>4</sup> originally prepared **1** by dissolving 'molybdenum(V) hydroxide' {prepared from  $(\text{NH}_4)_2[\text{MoOCl}_5]$  and  $(\text{NH}_4)_2\text{CO}_3$ } in concentrated formic acid and neutralizing the solution by addition of solid  $(\text{NH}_4)_2\text{CO}_3$ . Although our method does not involve a chloride-free intermediate, the presence of chloride impurities cannot, even in the crude product, be detected with silver nitrate. If **1** is prepared by our method but without the presence of formic acid in a sufficient concentration it will become contaminated with an orange X-ray-amorphous powder believed<sup>4</sup> to be a basic salt. The impurity may explain why Rosenheim and Nernst<sup>5</sup> did not obtain products that could be analysed correctly.

**Chemical properties.** When dry, **1** is not very sensitive to oxidation, and the crystals may be left in the atmosphere for weeks without any change in weight or appearance.



Even after several years no decomposition appears to have taken place. If **1** is dissolved in neutral water the orange amorphous substance mentioned above is formed. No precipitate is formed in 1 M formic acid.

A solution of **1** in 7 M (or 3.5 M) sodium formate which is 1 M with respect to formic acid has a UV-VIS spectrum (Fig. 1) which is believed to be that of  $[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]^{3-}$  (**2**). The spectrum in pure 1 M formic acid, i.e. with no sodium formate present, has an appearance intermediate between that of  $[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]^{3-}$  and  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ , indicating that partial aquation has taken place.

In dilute non-complexing strong acids, such as trifluoromethane sulfonic and perchloric acid, complete aquation of the formate complex immediately takes place and  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  may be identified by its UV-VIS spectrum<sup>7</sup> (Fig. 1).

A solution of  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  in 2 M  $\text{CF}_3\text{SO}_3\text{H}$  is stable when no dioxygen is present, but gradually loses its orange colour in the course of some weeks when exposed to the atmosphere. A solution of **1** in 1 M  $\text{HClO}_4$  has a constant UV-VIS spectrum for at least 3 months when no dioxygen

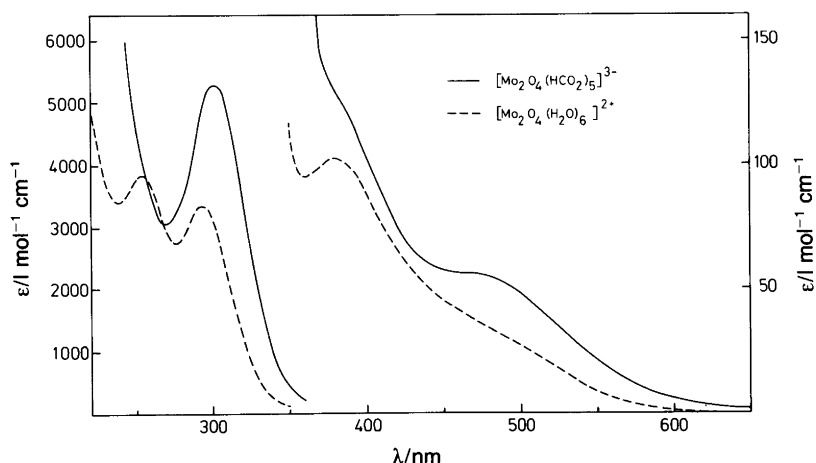


Fig. 1. UV-VIS absorption spectra of  $(\text{NH}_4)_3[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]$  in 5 M  $\text{Na}(\text{HCO}_2)/5$  M  $\text{HCO}_2\text{H}$  and in 1 M  $\text{HClO}_4$ . Under these conditions the absorbing species are believed to be  $[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]^{3-}$  and  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ , respectively. The strong absorbance by formate makes it impossible to observe  $[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]^{3-}$  bands below ca. 260 nm. Notice that the shape of the  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  absorption curve from 600 to 400 nm indicates the presence of an unresolved band around 500 nm. Spectral characteristics ( $\lambda/\text{nm}$ ,  $\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$ ) are as follows.  $[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]^{3-}$ : (470, 56)<sub>sh</sub>; (390, 121)<sub>sh</sub>; (302, 5280)<sub>max</sub>.  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$ : (385, 102)<sub>max</sub>; (296, 3330)<sub>max</sub>; (256, 3820)<sub>max</sub>. The data for  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  agree well with those previously reported.<sup>7,17,23</sup>

is present. In the atmosphere, however, such a solution may turn intensely blue after a couple of days. Concentrated (70 %) perchloric acid is observed within a total of 10 s to oxidize  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  first to a blue species and then to colourless  $\text{Mo}^{\text{VI}}$ . The rapidity of this oxidation may be due to the formation of mononuclear  $\text{Mo}^{\text{V}}$  which, unlike dinuclear  $\text{Mo}^{\text{V}}$ , has been found to react with perchlorate.<sup>11</sup> Note that  $[\text{MoO}(\text{HSO}_4)_5]^{2-}$  in conc.  $\text{H}_2\text{SO}_4$  (see below) is quickly oxidized by addition of a dilute solution of  $\text{HClO}_4$  in conc.  $\text{H}_2\text{SO}_4$ . A solution of **1** in 1 M  $\text{HNO}_3$  loses its orange colour as a result of oxidation within a day or so.

Compound **1** dissolves in 12 M hydrochloric acid under the immediate formation of a green solution containing the mononuclear complex  $[\text{MoOCl}_5]^{2-}$ . Dissolution of the compound in concentrated  $\text{H}_2\text{SO}_4$  (CO effervescence), concentrated  $\text{CF}_3\text{SO}_3\text{H}$  (CO effervescence) or 85 %  $\text{H}_3\text{PO}_4$  yields weakly coloured blue or blue–green solutions which have two absorption bands in the visible region that are very similar to the ligand field bands<sup>12</sup> of  $[\text{MoOCl}_5]^{2-}$ . It is thus highly likely that mononuclear oxomolybdenum(V) species are present in the concentrated acids. The species  $[\text{MoO}(\text{HSO}_4)_5]^{2-}$ <sup>13</sup> and  $[\text{MoO}(\text{H}_2\text{PO}_4)_4]^-$ <sup>14</sup> have been suggested. When the concentrated acids are diluted with water  $[\text{Mo}_2\text{O}_4]^{2+}$  is formed and the colours of the solutions change to orange.

Addition of  $\text{Eu}^{2+}(\text{aq})$  to a solution of  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  in 2 M trifluoromethane sulfonic or *p*-toluene sulfonic acid brings about immediate reduction to molybdenum(III), and  $[\text{Mo}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_8]^{4+}$  may be identified by its characteristic two-peak absorption band at 600 nm.<sup>15</sup> Such retention of dinuclearity in connection with redox reactions interconverting  $\text{Mo}^{\text{III}}$  and  $\text{Mo}^{\text{V}}$  seems to be a common feature of the aqueous chemistry of molybdenum.<sup>16</sup> However, when an excess of sodium formate is added to the reduced acidic ( $\text{CF}_3\text{SO}_3\text{H}$ ) solution some, but not all, molybdenum precipitates as  $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$ . Therefore, either mononuclear molybdenum(III) is formed as a biproduct in the redox process or  $[\text{Mo}_2(\mu\text{-OH})_2]^{4+}$  is able to monomerize in 7 M sodium formate.

When the green–yellow crystals of sodium hexakis(formato)molybdate(III) are exposed to the atmosphere they become oxidized on the surface and the original colour changes into brown–yellow within a couple of weeks.<sup>1</sup> The oxidized component may be extracted into saturated sodium formate solution, while pure green–yellow  $\text{Na}_3[\text{Mo}(\text{HCO}_2)_6]$  is left behind as an insoluble solid. The colour of the extract is red and it has a UV–VIS spectrum which is similar to that of **1**.

**Structure of the compound.** A crystal structure determination confirmed that the complex anion is binuclear (**2** and supplementary material) with two bridging oxygen atoms and a formate bridge, as determined independently by Kamenar *et al.*<sup>6</sup>

**Electronic spectra.** The overall appearances of the spectra of Fig. 1 are similar both to each other and to those of other

complexes of the *syn*- $[\text{Mo}_2\text{O}_4]^{2+}$  core (the edta,<sup>17</sup> taccd<sup>18</sup> and aqua-oxalato<sup>19</sup> complexes). The complexes all have a band of relatively low intensity ( $100 < \epsilon/\text{mol}^{-1} \text{cm}^{-1} < 400$ ) at 385–390 nm, an intense band ( $3500 < \epsilon/\text{mol}^{-1} \text{cm}^{-1} < 10000$ ) at 295–306 nm, and (if not obscured) and additional intense band of comparable intensity at 245–255 nm. In addition to the UV bands, the spectrum of  $[\text{Mo}_2\text{O}_4(\text{HCO}_2)_5]^{3-}$  contains a shoulder at 490 nm. A similar shoulder has been observed<sup>19</sup> for  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_2(\text{ox})_2]^{2-}$  [ $(\lambda, \epsilon)_{\text{sh}} = (490 \text{ nm}, 41 \text{ l mol}^{-1} \text{cm}^{-1})$ ], and inspection of the absorption curve of  $[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6]^{2+}$  reveals the presence of an unresolved band around 500 nm for that complex.

In considering the nature of the electronic transitions of *syn*- $[\text{Mo}_2\text{O}_4]^{2+}$  complexes one may examine the spectrum of the mononuclear complex  $[\text{MoOCl}_5]^{2-}$ . This has three absorption bands in the UV<sup>20</sup> [ $(\lambda/\text{nm}, \epsilon/\text{l mol}^{-1} \text{cm}^{-1})_{\text{max}} = (354, \approx 400), (311, \approx 5000) \text{ and } (240, \approx 5000)$ ] which Gray and Hare<sup>12</sup> originally assigned as being due to oxygen  $\rightarrow$  molybdenum charge transfer. However, the observation by Rudolf and Wolniak<sup>13</sup> that  $[\text{MoO}(\text{HSO}_4)_5]^{2-}$  had no bands in this wavelength region provided the basis for a reassignment of the three  $[\text{MoOCl}_5]^{2-}$  bands as due to chloride  $\rightarrow$  molybdenum charge transfer. Gray has agreed with this assignment in a more recent paper.<sup>14</sup> Support for the halogen  $\rightarrow$  molybdenum CT assignment may also be found by comparing the spectra of  $[\text{MoOCl}_5]^{2-}$  in 12 M HCl and  $[\text{MoOBr}_5]^{2-}$  in 9 M HBr: similar groups of three bands are found in both spectra, but for  $[\text{MoOBr}_5]^{2-}$  all three bands are red-shifted as compared to those of  $[\text{MoOCl}_5]^{2-}$ . For the first CT band this red shift amounts to ca.  $7000 \text{ cm}^{-1}$ . On the basis of the difference between the optical electro-negativities<sup>21</sup> of the two halides one may calculate the nearby value  $\Delta\sigma = 30000 \times [\chi_{\text{opt}}(\text{Cl}^-) - \chi_{\text{opt}}(\text{Br}^-)] = 30000 \times (3.0 - 2.8) = 6000 \text{ cm}^{-1}$ .

From the above it follows that all absorption bands of *syn*- $[\text{Mo}_2\text{O}_4]^{2+}$  complexes are associated with the  $[\text{Mo}_2\text{O}_4]^{2+}$  core as such and not with its mononuclear constituents. The bands may tentatively be assigned to excitations of an electron from the metal–metal  $\sigma$ -bonding molecular orbital<sup>22</sup> of *syn*- $[\text{Mo}_2\text{O}_4]^{2+}$  to higher-lying molecular orbitals.

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