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Structure and reactivity of an intermediate in the two-electron reduction of dimolybdenum(III) by a hydride ligand in the Mo–H–Mo system

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Abstract

The reaction between the μ-hydride dimolybdenum(III) complex $[Mo_2Cl_8H]^{3-}$ and carboxylic acids in aqueous solution produces a violet species which slowly decomposes to yield the quadruply bonded dimolybdenum(II) complex $Mo_2(O_2CR)_4$. The violet intermediate in the reaction of $[Mo_2Cl_8H]^{3-}$ with glycine was isolated by ion exchange chromatography and crystallized. The crystals of $[Mo_2H(OH)(gly)_2Cl_4]$ (**1**) are monoclinic, space group $P2_1/n$ with $a=9.536(4)$, $b=14.792(4)$, $c=9.339(3)$ Å, $\beta=109.99(3)°$, $V=1283(1)$ Å^3 and $Z=4$. The two Mo(III) ions in this complex are bridged by one hydride ligand, one OH^- group and two glycine groups through the carboxylic end. The Mo–Mo distance is 2.353(5) Å, the shortest found for the Mo–H–Mo system. $[(H_2O)_2MoH(OH)(gly)_2Mo(H_2O)_2]^{4+}$ is the structure proposed for the violet intermediate **II** in the reaction $4gly+[Mo_2Cl_8H]^{3-} \rightarrow II \rightarrow H^+ + [Mo_2(gly)_4]Cl_4+4Cl^-$. This structure was derived from structure **1**, the high ionic charge of about 4+ and the absence of chloride in this species. The decomposition reaction of **II** and the relation of **II** with the red intermediate **III** of the reaction $[Mo_2Cl_8H]^{3-}+H_2O \rightarrow III \rightarrow H_2+[Mo_2(OH)_2Cl_2]^{2+}+6Cl^-+H^+$ is discussed.

Keywords: Crystal structures; Molybdenum complexes; Hydride complexes; Binuclear complexes

1. Introduction

Over 25 years ago, Cotton and co-workers reported the preparation and structure of $Cs_3[Mo_2Cl_8H]$ (compound **I**) [1]. This remarkable compound, which contains a bridging hydride ligand, was prepared by heating tetraacetatedimolybdenum(II) in concentrated HCl:

$$Mo_2^{II}(O_2CCH_3)_4+5HCl+3CsCl \longrightarrow Cs_3[Mo_2Cl_8H]+4CH_3COOH \quad (1)$$

The anti-symmetric stretching frequency of Mo–H–Mo at 1245 cm^{-1} was shifted to 904 cm^{-1} in the deuterium-substituted compound $Cs_3[Mo_2Cl_8D]$ [1b]. The kinetics of reaction (1) and of the decomposition of **I** in acidic solutions were investigated by Miller and Haim [2]. Reaction (1) is, in fact, a two-electron reduction of an aquated proton by the two Mo(II) atoms:

$$2Mo(II)+H^+ \longrightarrow 2Mo(III)+H^-$$

This reaction may be reversed in aqueous solutions of acetate, glycinate and many other carboxylates and proceeds via a violet intermediate **II** [3]:

$$4RCOO^-+[Mo_2Cl_8H]^{3-} \longrightarrow II \longrightarrow H^++Mo_2(O_2CR)_4+8Cl^- \quad (2)$$

Heating of **II** in concentrated HCl reproduces $[Mo_2Cl_8H]^{3-}$ [3].

Species **II** with glycinate ($R=CH_2NH_3^+$) was separated from the reaction (2) mixture by ion-exchange chromatography [3]. The sharp violet band of **II** was eluted from the column by 3 M acids. It did not contain any coordinated chloride ions and its elution behavior indicated a 4+ charge [3]. It was found that the deep violet solutions of **II** underwent slow decomposition and produced the yellow end-product $Mo_2(OCR)_4$ [3,4]. No change in the oxidation numbers of Mo and H occurs in the reaction **I**→**II**. Furthermore, by the use of deuterated **I**, it was shown that the Mo–H–Mo bridging unit of **I** remained intact in **II** [3]. The breakdown of this structure and the accompanying electron transfer, $2Mo(III)+H^- \rightarrow 2Mo(II)+H^+$ occurs during the second step of reaction (2), $II \rightarrow H^+ + Mo_2(O_2CR)_4$.

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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Another decomposition reaction of **I**, in water or dilute mineral acids, in which the hydride or deuteride ligand reacts with H_2O to yield H_2 or HD, respectively, was reported by Cotton and Kalbacher [1b]. This reaction was later shown to proceed via a red intermediate **III**, a partial aquation product of **I**, in which the Mo(III)–H–Mo(III) unit is preserved [2,3]. This intermediate decomposes to yield H_2 and the Mo(III) dinuclear species $[Mo_2(OH)_2Cl_2(H_2O)_4]^{2+}$ [2,3].

$$[Mo_2Cl_8H]^{3-} + 2H_2O \longrightarrow \text{III} \longrightarrow H_2 + \{Mo_2(OH)_2Cl_2\}^{2+} + 6Cl^- + H^+ \quad (3)$$

The present study reports the composition and structure of the violet intermediate **II** with glycinate ligands and discusses some new aspects of the chemistry of reactions (1)–(3).

2. Experimental

2.1. Preparation of $[Mo_2H(OH)(gly)_2Cl_4]$ (1)

$Cs_3[Mo_2Cl_8H]$ (1 g, 1.14 mmol), prepared by a literature method [1a], was dissolved in 100 ml of 1 M glycine. The solution was stirred for 20 min and adsorbed on an ice-cooled cation-exchange column (DOWEX 50W-X2). The deep violet species was eluted with 3 M HCl and the dark violet eluate was kept at 0 °C. After 24 h small grey prisms of **1** were deposited. The crystals were collected and washed with cold water, acetone and ethyl ether.

2.2. X-ray crystallography

A crystal of **1** of dimensions 0.07×0.08×0.05 mm was attached to the end of a glass fiber and mounted on a CAD4 diffractometer. Cu Kα ($\lambda = 1.5418$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 20 reflections in the range of $20 < \theta < 28°$. Data were measured at 22 °C by using an ω–2θ motion. Lorentz and polarization corrections were applied. Intensity data were corrected for absorption using the ψ-scan method. The heavy atom positions were obtained by using the results of SHELX86 direct method analysis. The structure was refined[1] to convergence using anisotropic thermal parameters for all molybdenum and chlorine atoms and isotropic ones for all oxygen, nitrogen and carbon atoms. All the hydrogen atoms of the glycine ligands were introduced in calculated positions using the riding model. The hydride hydrogen atom was located from the difference map and introduced in a fixed position with $B = 0.5$.

3. Results and discussion

The crystallographic data for **1** are given in Table 1. The atomic positional parameters are listed in Table 2. Table 3 presents the important bond lengths and angles and Fig. 1 shows the numbering scheme in **1**. With $Z = 4$ in the cell of space group $P2_1/n$ there is no crystallographic symmetry imposed upon the complex. The two Mo(III) ions in **1** are bridged by one OH^- group, one H^- ligand and two glycine ligands which appear in their zwitterionic form and are co-

Table 1
Crystallographic data for $[Mo_2H(OH)(gly)_2Cl_4]$ (1)

Formula	$C_4H_{12}Cl_4Mo_2N_2O_5$
Formula weight	501.84
Space group	$P2_1/n$
a (Å)	9.536(4)
b (Å)	14.792(4)
c (Å)	9.339(3)
β (°)	102.99(3)
V (Å^3)	1283(1)
Z	4
ρ_{calc} (g cm^{-3})	2.596
μ (cm^{-1})	243.96
Range of 2θ (°)	4–110
No. unique data	1677
Data with $F_o^2 > 3\sigma(F_o^2)$	667
No. variables	99
R	0.086
R_w	0.094

Table 2
Positional parameters and e.s.d.s [a] for **1**

Atom	x	y	z
Mo(1)	0.7404(7)	0.3940(2)	0.6160(5)
Mo(2)	0.7615(7)	0.3652(2)	0.3739(5)
Cl(1)	0.554(2)	0.4277(8)	0.751(2)
Cl(2)	0.924(2)	0.4039(8)	0.836(2)
Cl(3)	0.963(2)	0.3403(8)	0.267(2)
Cl(4)	0.597(2)	0.3569(7)	0.128(1)
O(1)	0.563(4)	0.380(2)	0.434(3)
O(2)	0.727(4)	0.254(2)	0.649(4)
O(3)	0.751(4)	0.226(1)	0.413(3)
O(4)	0.746(4)	0.531(2)	0.563(4)
O(5)	0.782(3)	0.507(1)	0.354(3)
N(1)	0.755(4)	0.045(2)	0.464(4)
N(2)	0.700(5)	0.708(2)	0.535(5)
C(1)	0.716(8)	0.205(4)	0.544(8)
C(2)	0.746(6)	0.104(3)	0.578(5)
C(3)	0.763(6)	0.570(3)	0.448(5)
C(4)	0.767(7)	0.664(3)	0.413(5)
H(1)	0.8904	0.3570	0.5264

[a] E.s.d.s in the least significant digits are shown in parentheses.

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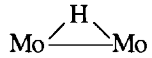
[1] All crystallographic computing was done on a VAX 9000 computer at the Hebrew University, using the TEXSAN structure determination package.

Table 3
Important bond lengths (Å) and angles (°) for 1

Atom	Atom	Distance	Atom	Atom	Distance
Mo(1)	Mo(2)	2.353(5)	Mo(2)	Cl(3)	2.39(2)
Mo(1)	Cl(1)	2.44(2)	Mo(2)	Cl(4)	2.48(2)
Mo(1)	Cl(2)	2.39(2)	Mo(2)	O(1)	2.10(3)
Mo(1)	O(1)	2.12(3)	Mo(2)	O(3)	2.10(2)
Mo(1)	O(2)	2.11(3)	Mo(2)	O(5)	2.12(2)
Mo(1)	O(4)	2.10(3)	Mo(2)	H(1)	1.66
Mo(1)	H(1)	1.89			

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Mo(2)	Mo(1)	Cl(1)	139.4(4)	Mo(1)	Mo(2)	Cl(4)	136.6(4)
Mo(2)	Mo(1)	Cl(2)	129.4(5)	Mo(1)	Mo(2)	O(1)	56.5(9)
Mo(2)	Mo(1)	O(1)	55.6(9)	Mo(1)	Mo(2)	O(3)	89.5(8)
Mo(2)	Mo(1)	O(2)	89.0(9)	Mo(1)	Mo(2)	O(5)	86.3(7)
Mo(2)	Mo(1)	O(4)	86(1)	Mo(1)	Mo(2)	H(1)	52
Mo(2)	Mo(1)	H(1)	44	Cl(3)	Mo(2)	Cl(4)	90.3(6)
Cl(1)	Mo(1)	Cl(2)	91.2(6)	Cl(3)	Mo(2)	O(1)	170(1)
Cl(1)	Mo(1)	O(1)	84(1)	Cl(3)	Mo(2)	O(3)	90(1)
Cl(1)	Mo(1)	O(2)	93(1)	Cl(3)	Mo(2)	O(5)	90.9(9)
Cl(1)	Mo(1)	O(4)	89(1)	Cl(3)	Mo(2)	H(1)	80
Cl(1)	Mo(1)	H(1)	173	Cl(4)	Mo(2)	O(1)	80(1)
Cl(2)	Mo(1)	O(1)	174(1)	Cl(4)	Mo(2)	O(3)	93.9(9)
Cl(2)	Mo(1)	O(2)	90(1)	Cl(4)	Mo(2)	O(5)	91.1(9)
Cl(2)	Mo(1)	O(4)	95(1)	Cl(4)	Mo(2)	H(1)	169
Cl(2)	Mo(1)	H(1)	85	O(1)	Mo(2)	O(3)	88(1)
O(1)	Mo(1)	O(2)	87(1)	O(1)	Mo(2)	O(5)	92(1)
O(1)	Mo(1)	O(4)	88(1)	O(1)	Mo(2)	H(1)	108
O(1)	Mo(1)	H(1)	99	O(3)	Mo(2)	O(5)	175(1)
O(2)	Mo(1)	O(4)	175(1)	O(3)	Mo(2)	H(1)	80
O(2)	Mo(1)	H(1)	81	O(5)	Mo(2)	H(1)	94
O(4)	Mo(1)	H(1)	96	Mo(1)	O(1)	Mo(2)	68(1)
Mo(1)	Mo(2)	Cl(3)	133.0(4)	Mo(1)	H(1)	Mo(2)	82

ordinated through their carboxylic oxygen atoms. In addition, each molybdenum atom is coordinated to two Cl^- ligands, completing a distorted octahedral geometry. The Mo–Mo distance in this edge-sharing bioctahedral complex, 2.353(5) Å, is significantly shorter than in some Mo(III)–μ(OH)$_2$–Mo(III) complexes with distances in the range 2.430(3)–2.501(3) Å [5]. However, this distance is only slightly shorter than the Mo–Mo distances in the face-sharing $[Mo_2X_8H]^{3-}$ complexes: X = Cl, 2.377(7) Å; X = Br, 2.384(4) Å and X = I, 2.408(2) Å [6,7]. The small variation in Mo–Mo distances in all hydride-bridged compounds is predicted by theoretical studies suggesting that the



core is a three-center four-electron system with a strong interaction [6]. The relatively short Mo–Mo distance in 1 causes a decrease in the Mo–O(H)–Mo angle to 68(1)°, as compared with values in the range of 72–73° found in several Mo(III)–μ-(OH)$_2$ – Mo(III) systems [5].

The two NH_3^+ groups in 1 participate in the formation of intramolecular hydrogen bonds to the O(4) and O(3) atoms of the bridging carboxyl groups with O(4)···N(2) and O(3)···N(1) separations of 2.66(4) and 2.72(3) Å, respectively. Similar interactions are found in several other compounds with bridging $^-O_2CCH_2NH_3^+$ ligands [4,8].

3.1. Composition of II

The structure of the violet intermediate **II** of reaction (2) is deduced from three experimental results:

(a) The violet band of **II**, eluted from the ion-exchange column, by 3 M acids (H_2SO_4 or *p*-toluenesulfonic acid) does not contain any coordinated chloride [3].

(b) The slow elution of **II** by these concentrations of acids indicates a high ionic charge of about 4+.

(c) **II** reacts slowly with chloride ions to form the sparingly soluble neutral complex $[Mo_2H(OH)(gly)_2Cl_4]$ (**1**).

These results support the conclusion that **II** is the tetrapositive complex ion $[(H_2O)_2MoH(OH)(gly)_2Mo(H_2O)_2]^{4+}$, an inert Mo(III) complex in which the

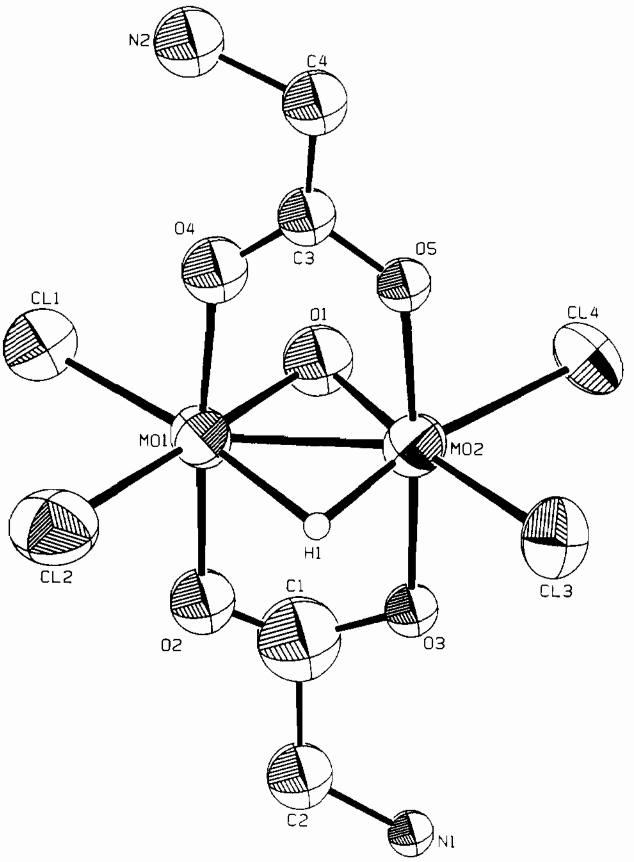


Fig. 1. Structure of $[Mo_2H(OH)(gly)_2Cl_4]$ (**1**).

four aqua ligands are slowly substituted by chloride ions to yield compound **1**.

*3.2. Decomposition of **II** to tetraglycinatedimolybdenum (II)*

While **II** contains two Mo(III) atoms and *two* bridging glycinates (as well as bridging hydride and hydroxide ligands), the end product contains two Mo(II) atoms and *four* glycinates. Therefore, the decomposition reaction of **II**:

$$2\{Mo_2H(OH)(gly)_2\}^{4+} \longrightarrow [Mo_2(gly)_4]^{4+} + Mo_2(aq)^{4+} + H_2O$$

involves a redox step, $2Mo(III) + H^- \rightarrow 2Mo(II) + H^+$ and a ligand transfer step. These processes may take place simultaneously in one intermolecular step or in two (or more) steps; the first is the redox reaction, which may be intramolecular.

*3.3. Relation between the reaction intermediates **II** and **III***

A common structural feature of the violet intermediate **II** and the red intermediate **III** is that both retain the Mo(III)–H–Mo(III) bridging unit of **I**. The structural data of **1** reported here and the kinetic data of Miller and Haim [2] support the view that a bridging OH ligand is another common feature of these two intermediates, i.e. both possess the Mo(III)H(OH)-Mo(III) unit. The Mo(III)H(OH)Mo(III) or Mo(III)H-(OH)ClMo(III) unit of the red intermediate **III** [3] breaks down spontaneously by a reaction with H_2O (reaction (3)) *unless* carboxylate ions are present in solution. Such carboxylate ions convert **III** into **II** and thereby block the decomposition reaction path. Under these conditions the slower two-electron redox reaction, between the two Mo(III) atoms and the hydride ligand, takes place (reaction (2)). The assumption that **III** is the first intermediate formed in both reactions (2) and (3) is supported by the observation that the red **III** is converted to the violet **II** ion by the addition of carboxylate ions.

4. Supplementary material

Tables of positional and thermal parameters, bond distances and angles, calculated positions of hydrogen atoms, intermolecular distances and structure factors for **1** (11 pages) are available from author A.B.

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