

Contribution from the Department of Chemistry,  
Texas A&M University, College Station, Texas 77843

## Polymorphs of Tetrakis(glycine)tetrachlorodimolybdenum(II)

AVI BINO, F. ALBERT COTTON,\* and PHILLIP E. FANWICK

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The compound  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot x\text{H}_2\text{O}$  has been obtained in two different crystalline forms, each of which has been structurally characterized by X-ray crystallography. Form **1** has  $x = 3$  and crystallizes in the space group  $P2_1/c$  with the following unit cell dimensions:  $a = 8.350$  (3) Å,  $b = 9.346$  (3) Å,  $c = 14.807$  (4) Å,  $\beta = 103.42$  (3)°,  $V = 1124$  (1) Å<sup>3</sup>,  $Z = 2$ . Form **2** has  $x = 2.67$  and crystallizes in the space group  $P\bar{1}$  with unit cell dimensions of  $a = 11.941$  (9) Å,  $b = 12.022$  (9) Å,  $c = 11.614$  (9) Å,  $\alpha = 92.42$  (7)°,  $\beta = 92.04$  (7)°,  $\gamma = 88.94$  (7)°,  $V = 1664$  (4) Å<sup>3</sup>,  $Z = 3$ . In **1** there are two equivalent  $\text{Mo}_2(\text{gly})_4^{4+}$  ions per unit cell, each located on a crystallographic center of symmetry, with  $d(\text{Mo} \cdots \text{Mo}) = 2.112$  (1) Å. There is weak axial coordination of  $\text{Cl}^-$ , with  $d(\text{Mo} \cdots \text{Cl}) = 2.882$  (1) Å. In **2**, there are three crystallographically independent molecules, each residing on a crystallographic inversion center. These have Mo-Mo distances of 2.107 (1), 2.110 (1), and 2.103 (1) Å and Mo $\cdots$ Cl distances of 2.907 (1), 2.869 (2), and 2.829 (2) Å, in the same order. In all four crystallographically independent  $\text{Mo}_2(\text{gly})_4\text{Cl}_4$  units the dimensions are thus effectively the same, and in all four there is virtual  $D_{4h}$  symmetry. Those  $\text{Cl}^-$  ions not loosely coordinated to the  $\text{Mo}_2(\text{gly})_4^{4+}$  units are hydrogen bonded to  $\text{NH}_3^+$  and  $\text{H}_2\text{O}$ .

## Introduction

Several years ago, when the study of amino acid complexes of the  $\text{Mo}_2^{4+}$  unit was initiated,<sup>1</sup> the first compound obtained was  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot x\text{H}_2\text{O}$ , in which gly represents the zwitterionic form of glycine,  $^+\text{H}_3\text{NCH}_2\text{CO}_2^-$ , and  $x$  was approximately 3. At that time the composition of the compound did not appear, from elemental analyses, to be completely reproducible, and crystals suitable for single-crystal X-ray study were not obtained. Instead, the chloride was converted to the sulfate  $\text{Mo}_2(\text{gly})_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  which gives excellent crystals<sup>1</sup> and whose structure lent itself admirably to single-crystal spectroscopy.<sup>2</sup>

In the meantime a study<sup>3</sup> of the reactions of the  $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$  and  $\text{Mo}_2\text{Cl}_8\text{D}^{3-}$  ions with carboxylic acids showed that the ultimate product of the reaction of glycine with  $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$  in cold 3 M HCl is a gray-violet substance having an elemental analysis consistent with the formula  $[\text{Mo}_2(\text{gly})_2\text{H}]\text{Cl}_4 \cdot 3\text{H}_2\text{O}$ , with some possible uncertainty as to whether one of the assigned  $\text{H}_2\text{O}$ 's might not actually be  $\text{OH}^-$ . The retention of the H ligand was proved by making the deuterium analogue from  $\text{Cs}_3\text{Mo}_2\text{Cl}_8\text{D}$  and showing that this could be converted back to  $\text{Cs}_3\text{Mo}_2\text{Cl}_8\text{H}$  by treatment with excess HCl and CsCl. Unfortunately, in this case also, crystals suitable for an X-ray structure analysis were not obtained.

Renewed interest<sup>4</sup> in the amino acid and peptide complexes of  $\text{Mo}_2^{4+}$  has led us to reexamine the above compounds containing glycine ligands and chloride. We now find that good single crystals of  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot x\text{H}_2\text{O}$  are obtained, not only in one form but in two. We have determined the structures of both of these forms and report those and other results in detail here.

## Experimental Section

**Preparations.  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 3\text{H}_2\text{O}$  (1).** One hundred milligrams of  $\text{K}_4\text{Mo}_2\text{Cl}_8$ , prepared by a literature method,<sup>5</sup> was dissolved in 50 mL of an aqueous solution (0.5 M) of glycine. The resulting yellow solution was allowed to mix by diffusion through a glass frit with a 2 M solution of hydrochloric acid at ca. 25 °C. Yellow crystals were formed over a period of 24 h.

**$\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$  (2).** Two hundred milligrams of  $\text{Cs}_3\text{Mo}_2\text{Cl}_8\text{H}$ , prepared by a literature method,<sup>6</sup> was dissolved in 50 mL of an aqueous solution (1 M) of glycine. After 15 min at about 20 °C the color of the solution became violet, as described previously.<sup>3</sup> The violet species was absorbed on a cation-exchange column (Dowex 50W-X2) and then eluted with 1 M HCl solution. The eluate was stored at 0 °C under  $\text{N}_2$ . After 24 h the color of the solution had become yellow-brown and yellow crystals had formed.

Table I. Crystallographic Data

	$\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 3\text{H}_2\text{O}$ (1)	$\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 2\frac{2}{3}\text{H}_2\text{O}$ (2)
space group	$P2_1/c$	$P\bar{1}$
$a$ , Å	8.350 (3)	11.941 (9)
$b$ , Å	9.346 (3)	12.022 (9)
$c$ , Å	14.807 (4)	11.614 (9)
$\alpha$ , deg	90.0	92.42 (7)
$\beta$ , deg	103.42 (3)	92.04 (7)
$\gamma$ , deg	90.0	88.94 (7)
$V$ , Å <sup>3</sup>	1124 (1)	1664 (4)
$d$ , g/cm <sup>3</sup>	2.03	2.06
$Z$	2	3
crystal size, mm	0.08 × 0.08 × 0.1	0.15 × 0.15 × 0.1
$\mu$ , cm <sup>-1</sup>	16.4	16.4
no. of unique data	1149	3903
data with $F_o^2 > 3\sigma(F_o^2)$	1121	3551
$R_1$ (anisotropic)	0.038	0.047
$R_2$ (anisotropic)	0.056	0.069
goodness of fit	1.34	1.67

**X-Ray Crystallography. Collection of Data.** Data were collected for both compounds on a Syntex  $P\bar{1}$  automated four-circle diffractometer by using Mo ( $\lambda$  0.71073 Å) radiation with a graphite crystal monochromator in the incident beam. Rotation photographs and  $\omega$  scans of several strong reflections indicated in each case that the crystals were of satisfactory quality. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range  $25^\circ < 2\theta < 45^\circ$ . Data were collected at  $22 \pm 3$  °C by using  $\theta$ - $2\theta$  scan technique with a variable scan rate from 4.0 to 24.0°/min. General procedures for data collection have been reported elsewhere.<sup>7</sup> Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. No absorption correction was applied.

**Solution and Refinement of the Structures.**<sup>4</sup> The heavy-atom positions in **1** were obtained through a three-dimensional Patterson function. This structure was refined in space group  $P2_1/c$  to convergence with anisotropic thermal parameters for all atoms except O(W2). The heavy-atom positions in **2** were obtained by direct methods with the MULTAN program. This structure was refined in space group  $P\bar{1}$  to convergence by using anisotropic thermal parameters for all atoms. The final discrepancy indices defined as

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_2 = \frac{[\sum w(|F_o| - |F_c|)^2]^{1/2}}{\sum w|F_o|}$$

are listed in Table I. The final difference maps showed no peaks of structural significance.

## Results and Discussion

The atomic positional and thermal parameters are presented

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for Monoclinic  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 3\text{H}_2\text{O}^a$ 

atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Mo(1)	0.05651 (7)	0.10006 (7)	-0.00437 (4)	1.77 (2)	1.36 (2)	1.66 (2)	-0.11 (2)	0.78 (2)	0.09 (2)
Cl(1)	0.2079 (2)	0.3782 (2)	0.0030 (1)	2.33 (7)	2.21 (8)	2.40 (7)	-0.32 (6)	0.91 (6)	-0.17 (6)
Cl(2)	0.6791 (3)	-0.6474 (4)	0.1688 (2)	3.0 (1)	7.2 (2)	6.2 (1)	0.2 (1)	0.93 (9)	2.3 (1)
O(1)	0.0648 (6)	0.0640 (5)	-0.1450 (3)	2.8 (2)	1.7 (2)	1.9 (2)	-0.4 (2)	1.1 (2)	-0.0 (2)
O(2)	0.0542 (6)	0.1476 (6)	0.1351 (3)	3.0 (2)	1.6 (2)	1.8 (2)	-0.3 (2)	0.9 (2)	-0.1 (2)
O(3)	0.2935 (6)	0.0076 (5)	0.0367 (4)	1.6 (2)	1.5 (2)	3.1 (2)	0.0 (2)	0.5 (2)	0.2 (2)
O(4)	0.1750 (6)	-0.2044 (5)	0.0452 (3)	1.8 (2)	1.9 (2)	2.8 (2)	0.1 (2)	0.9 (2)	0.3 (2)
Ow(1)	0.4074 (13)	-0.4568 (17)	0.2409 (8)	13.2 (6)	21 (1)	10.9 (6)	9.4 (7)	6.6 (5)	6.4 (7)
Ow(2)	0.365 (3)	0.247 (3)	0.227 (2)	10.8 (7)					
N(1)	0.0403 (8)	0.0372 (7)	-0.3314 (4)	4.0 (3)	2.6 (3)	2.1 (2)	-0.6 (3)	1.6 (2)	0.2 (2)
N(2)	0.4585 (8)	-0.3502 (8)	0.0684 (6)	3.1 (3)	2.0 (3)	6.3 (4)	0.7 (3)	2.0 (3)	0.2 (3)
C(11)	0.0064 (9)	-0.0534 (8)	-0.1799 (5)	2.4 (3)	1.7 (3)	1.9 (3)	0.3 (3)	0.7 (2)	0.3 (3)
C(12)	-0.0079 (11)	0.0926 (9)	0.2779 (5)	5.1 (4)	2.4 (4)	1.4 (3)	-0.4 (3)	1.1 (3)	0.2 (3)
C(21)	0.2981 (9)	-0.1261 (9)	0.0481 (5)	1.9 (3)	2.9 (4)	2.0 (3)	0.1 (3)	0.7 (2)	0.1 (3)
C(22)	0.4704 (10)	-0.1937 (10)	0.0648 (7)	3.0 (4)	2.4 (4)	5.8 (5)	0.6 (3)	1.1 (3)	0.2 (4)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}kib^*c^*)]$ .

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for Triclinic  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 2^{1/3}\text{H}_2\text{O}^a$ 

atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Mo(1)	0.46197 (6)	0.98241 (6)	0.07753 (6)	1.83 (3)	1.93 (3)	1.57 (3)	0.16 (2)	-0.13 (2)	0.08 (2)
Mo(2)	-0.07412 (6)	0.54503 (6)	-0.02085 (6)	1.78 (3)	1.46 (3)	1.46 (3)	0.14 (2)	-0.15 (2)	0.04 (2)
Mo(3)	-0.00435 (6)	0.92319 (6)	-0.54658 (6)	1.97 (3)	1.34 (3)	1.39 (3)	-0.07 (2)	-0.12 (2)	-0.11 (2)
Cl(1)	0.3680 (2)	0.9866 (2)	0.3052 (2)	3.6 (1)	3.5 (1)	2.38 (9)	-0.45 (8)	0.14 (8)	0.34 (8)
Cl(2)	-0.2927 (2)	0.6476 (2)	-0.0354 (2)	2.63 (9)	2.88 (9)	3.06 (9)	0.39 (8)	-0.42 (8)	0.32 (8)
Cl(3)	0.0054 (2)	0.7085 (2)	-0.6556 (2)	3.25 (9)	1.92 (8)	2.16 (8)	-0.10 (7)	-0.51 (7)	-0.08 (7)
Cl(4)	0.8256 (2)	0.1963 (2)	0.1857 (2)	3.4 (1)	3.4 (1)	3.0 (1)	-0.12 (9)	-0.58 (8)	-0.03 (9)
Cl(5)	0.2934 (3)	0.6178 (2)	0.4547 (3)	4.8 (1)	3.7 (1)	7.1 (2)	-0.2 (1)	1.4 (1)	0.8 (1)
Cl(6)	0.6400 (3)	0.7561 (3)	0.4429 (4)	5.8 (2)	5.1 (2)	10.0 (2)	-0.8 (1)	-0.1 (2)	0.9 (2)
Ow(1)	-0.1685 (6)	0.6145 (6)	-0.4218 (6)	4.1 (3)	4.0 (3)	3.7 (3)	-0.6 (3)	-0.2 (3)	-0.4 (3)
Ow(2)	0.3928 (7)	0.5963 (7)	0.1592 (8)	5.0 (4)	4.5 (4)	7.0 (5)	0.3 (3)	-1.0 (4)	0.5 (4)
Ow(3)	0.4461 (11)	0.4088 (14)	0.3700 (10)	14.4 (8)	21 (1)	8.3 (6)	5.9 (8)	6.9 (5)	0.3 (7)
Ow(4)	0.6023 (7)	0.5601 (8)	0.2701 (8)	5.5 (4)	7.4 (5)	7.7 (5)	1.7 (4)	0.1 (4)	-1.2 (4)
O(11)	0.6144 (5)	0.9188 (5)	0.1476 (5)	2.3 (2)	2.3 (2)	2.0 (2)	0.4 (2)	0.2 (2)	0.2 (2)
O(12)	0.3029 (4)	1.0422 (5)	0.0156 (5)	1.8 (2)	2.6 (2)	2.1 (2)	0.4 (2)	-0.2 (2)	0.1 (2)
O(13)	0.4993 (5)	1.1437 (5)	0.1466 (5)	2.7 (2)	2.4 (3)	2.6 (3)	-0.0 (2)	0.2 (2)	-0.4 (2)
O(14)	0.4175 (5)	0.8201 (5)	0.0174 (5)	2.6 (2)	2.0 (2)	3.0 (3)	-0.1 (2)	-0.2 (2)	0.6 (2)
O(21)	0.1527 (4)	0.6029 (5)	0.0821 (5)	2.2 (2)	2.0 (2)	2.4 (2)	-0.0 (2)	-0.6 (2)	-0.5 (2)
O(22)	-0.0043 (4)	0.6982 (4)	0.0385 (5)	1.8 (2)	1.9 (2)	2.0 (2)	0.4 (2)	-0.3 (2)	-0.3 (2)
O(23)	-0.0225 (4)	0.5755 (4)	-0.1896 (4)	2.2 (2)	2.0 (2)	1.4 (2)	0.2 (2)	0.2 (2)	0.4 (2)
O(24)	0.1353 (5)	0.4806 (5)	-0.1467 (5)	2.3 (2)	2.2 (2)	1.8 (2)	0.0 (2)	0.1 (2)	0.4 (2)
O(31)	0.1656 (4)	0.8838 (4)	-0.4947 (5)	2.2 (2)	1.9 (2)	1.8 (2)	0.4 (2)	-0.2 (2)	-0.2 (2)
O(32)	-0.0575 (5)	1.0090 (4)	-0.3017 (5)	3.4 (3)	1.1 (2)	1.9 (2)	-0.1 (2)	0.5 (2)	0.0 (2)
O(33)	-0.1698 (4)	0.9545 (4)	-0.6062 (5)	2.1 (2)	1.7 (2)	2.6 (2)	0.2 (2)	-0.3 (2)	-0.6 (2)
O(34)	-0.0689 (5)	0.8465 (5)	-0.4015 (5)	2.6 (2)	1.9 (2)	2.1 (2)	-0.1 (2)	0.4 (2)	-0.0 (2)
N(11)	0.7853 (7)	0.7784 (6)	0.2062 (6)	4.0 (4)	2.6 (3)	2.7 (3)	1.3 (3)	-1.2 (3)	-0.4 (3)
N(12)	0.3411 (8)	0.6206 (8)	-0.0834 (8)	4.6 (4)	4.0 (4)	5.0 (4)	-1.1 (3)	0.3 (4)	0.1 (4)
N(21)	0.2324 (7)	0.7716 (7)	0.2229 (7)	3.4 (3)	3.2 (3)	2.9 (3)	-0.9 (3)	-0.3 (3)	-0.5 (3)
N(22)	0.0727 (6)	0.6497 (6)	-0.3874 (6)	3.9 (3)	2.3 (3)	1.9 (3)	0.1 (3)	0.0 (3)	0.7 (3)
N(31)	0.3927 (7)	0.8513 (7)	-0.4653 (7)	2.8 (3)	3.8 (4)	4.3 (4)	0.8 (3)	-0.2 (3)	0.0 (3)
N(32)	-0.2283 (7)	0.7830 (7)	-0.2502 (7)	3.5 (3)	3.0 (3)	3.7 (4)	-0.8 (3)	0.9 (3)	0.2 (3)
C(11)	0.6990 (7)	0.9187 (7)	0.0839 (7)	2.2 (3)	2.3 (3)	2.0 (3)	0.3 (3)	-0.6 (3)	-0.2 (3)
C(12)	0.8080 (8)	0.8743 (8)	0.1326 (7)	3.4 (4)	3.2 (4)	1.9 (4)	0.7 (3)	-0.8 (3)	0.1 (3)
C(13)	0.5492 (7)	1.2080 (7)	0.0867 (8)	2.1 (3)	2.4 (4)	3.5 (4)	0.4 (3)	-1.1 (3)	-0.8 (3)
C(14)	0.5700 (8)	1.3228 (8)	0.1386 (10)	3.2 (4)	2.3 (4)	6.2 (6)	-0.5 (3)	0.7 (4)	-0.9 (4)
C(21)	0.0942 (7)	0.6934 (7)	0.0785 (7)	3.4 (4)	1.9 (3)	1.0 (3)	-0.3 (3)	0.2 (3)	-0.3 (3)
C(22)	0.1529 (8)	0.7989 (7)	-0.1226 (7)	3.2 (4)	2.3 (4)	2.3 (4)	-0.6 (3)	-0.5 (3)	-0.0 (3)
C(23)	0.0727 (7)	0.5356 (7)	-0.2148 (7)	3.1 (4)	2.0 (3)	1.6 (3)	-0.5 (3)	-0.0 (3)	0.0 (3)
C(24)	0.1179 (8)	0.5481 (7)	-0.3340 (7)	3.6 (4)	2.0 (3)	1.6 (3)	0.2 (3)	0.6 (3)	0.1 (3)
C(31)	-0.2155 (7)	1.0439 (7)	-0.5703 (7)	1.9 (3)	2.5 (3)	2.2 (3)	-0.8 (3)	-0.2 (3)	0.4 (3)
C(33)	0.3387 (8)	0.9349 (8)	-0.3915 (8)	2.9 (4)	3.4 (4)	2.8 (4)	0.7 (3)	-0.8 (3)	-0.9 (3)
C(32)	-0.0839 (7)	0.9080 (7)	-0.3103 (7)	1.8 (3)	2.6 (4)	1.9 (3)	0.6 (3)	-0.1 (3)	0.1 (3)
C(34)	-0.1321 (8)	0.8558 (7)	-0.2084 (8)	3.6 (4)	2.4 (4)	2.4 (4)	-0.4 (3)	0.6 (3)	0.6 (3)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}kib^*c^*)]$ .

in Tables II and III for the monoclinic (**1**) and triclinic (**2**) forms, respectively, of  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot x\text{H}_2\text{O}$ . Figures 1 and 2 show the  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  units in **1** and **2**, respectively, and define the atom numbering. For **1**, where there is only half a molecule in the asymmetric unit, with the other half related to it by a crystallographic inversion center, atoms related by the inversion operation are given the same designation except

for the addition of a prime to one of them. For the three independent centric molecules of **2**, packed as shown in Figure 3, we use a scheme that allows Figure 2 to define the numbering for all three. Figure 2 shows the  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  unit containing metal atoms Mo(1) and Mo(1)' and chlorine atoms Cl(1) and Cl(1)'. All other atoms in this unit have numbers that begin with 1. In the  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  unit containing

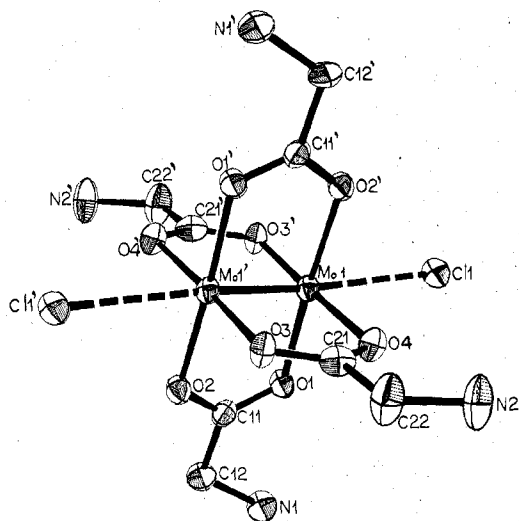


Figure 1. An ORTEP drawing of the  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  unit in compound 1. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density.

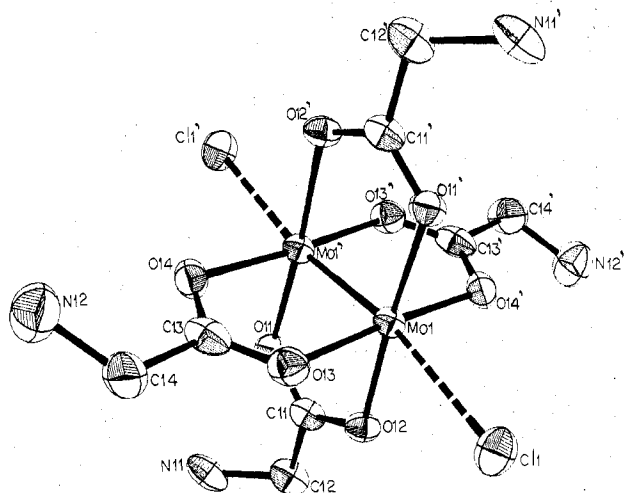


Figure 2. An ORTEP drawing of one of the three independent  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  units in compound 2. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 40% of the electron density. The numbering scheme shown for this unit implicitly defines the numbering in the other two, as explained in the text.

$\text{Mo}(2)$  and  $\text{Cl}(2)$  all other atoms have numbers beginning with 2, and a similar scheme is used for the third  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  unit.

Table IV gives interatomic distances and angles for 1 and

Table IV. Bond Distances and Bond Angles for Monoclinic  $\text{Mo}_2(\text{gly})_4\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (1) (Tetrakis(glycine)dimolybdenum Tetrachloride Trihydrate)

Bond Distances, Å			
$\text{Mo}(1)-\text{Mo}(1)'$	2.112 (1)		
$-\text{Cl}(1)$	2.882 (1)		
$-\text{O}(1)$	2.126 (4)		
$-\text{O}(2)'$	2.116 (4)		
$-\text{O}(3)'$	2.115 (4)		
$-\text{O}(4)$	2.124 (4)		
$\text{O}(1)-\text{C}(11)$	1.262 (8)	$\text{O}(3)-\text{C}(21)$	1.260 (9)
$\text{O}(2)-\text{C}(11)$	1.275 (8)	$\text{O}(4)-\text{C}(21)$	1.255 (8)
$\text{C}(11)-\text{C}(12)$	1.50 (1)	$\text{C}(21)-\text{C}(22)$	1.54 (1)
$\text{C}(12)-\text{N}(1)$	1.507 (9)	$\text{C}(22)-\text{N}(2)$	1.47 (1)

Bond Angles, Deg			
$\text{Mo}(1)'\text{-Mo}(1)\text{-Cl}(1)$	174.11 (5)	$\text{Mo}(1)\text{-O}(4)\text{-C}(21)$	115.2 (4)
$-\text{O}(1)$	92.1 (1)	$\text{Mo}(1)'\text{-O}(3)\text{-C}(21)$	116.2 (4)
$-\text{O}(2)'$	91.2 (1)	$\text{O}(3)\text{-C}(21)\text{-O}(4)$	125.0 (6)
$-\text{O}(3)'$	91.3 (1)	$\text{O}(3)\text{-C}(21)\text{-C}(22)$	115.3 (6)
$-\text{O}(4)$	92.0 (1)	$\text{O}(4)\text{-C}(21)\text{-C}(22)$	119.6 (7)
$\text{O}(1)\text{-Mo}(1)\text{-O}(2)'$	176.7 (2)	$\text{C}(21)\text{-C}(22)\text{-N}(2)$	110.3 (7)
$-\text{O}(3)'$	88.6 (2)	$\text{Mo}(1)\text{-O}(1)\text{-C}(11)$	116.2 (4)
$-\text{O}(4)$	91.6 (1)	$\text{Mo}(1)'\text{-O}(2)\text{-C}(11)$	117.2 (4)
$\text{O}(2)'\text{-Mo}(1)\text{-O}(3)'$	91.4 (2)	$\text{O}(1)\text{-C}(11)\text{-O}(2)$	123.3 (6)
$-\text{O}(4)$	88.2 (2)	$\text{O}(1)\text{-C}(11)\text{-C}(12)$	121.3 (6)
$\text{O}(3)'\text{-Mo}(1)\text{-O}(4)$	176.8 (2)	$\text{O}(2)\text{-C}(11)\text{-C}(12)$	115.4 (6)
		$\text{C}(11)\text{-C}(12)\text{-N}(1)$	110.8 (6)

Table V gives the same information for 2, following the numbering rules just stated. Thus, there are dimensions for four crystallographically independent  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  units, one in 1 and three in 2, presented in Tables IV and V. In Table VI we present the average values of the more important distances and angles, averaged over the four units.

The variations in Mo-Mo distances from one  $\text{Mo}_2$  unit to another are not statistically significant except for those between the value of 2.103 (1) Å and the two largest, viz., 2.110 (1) and 2.112 (1) Å. Even these differences, 0.007 (2) and 0.009 (2) Å, are so small that they presumably reflect slight differences in intermolecular interactions that are without chemical significance. The average of all four Mo-Mo distances, 2.108 Å, is only 0.007 Å shorter than that found in the sulfate. The other types of interatomic distance and the MoMoO angle vary only slightly and randomly over all four units and each of the mean values differs by much less than the uncertainty interval from the value (or average value) of the same distance or angle in the sulfate. In short, over five crystallographically independent  $\text{Mo}_2(\text{gly})_4^{4+}$  units, the dimensions show no variation that is chemically significant.

The formation of two different crystalline phases both containing the  $[\text{Mo}_2(\text{gly})_4\text{Cl}_2]^{2+}$  unit but having different structures and different water content is somewhat surprising. Presumably their stabilities are essentially the same and thus either can be formed, depending on the exact conditions of crystal formation. We do not, however, know what differ-

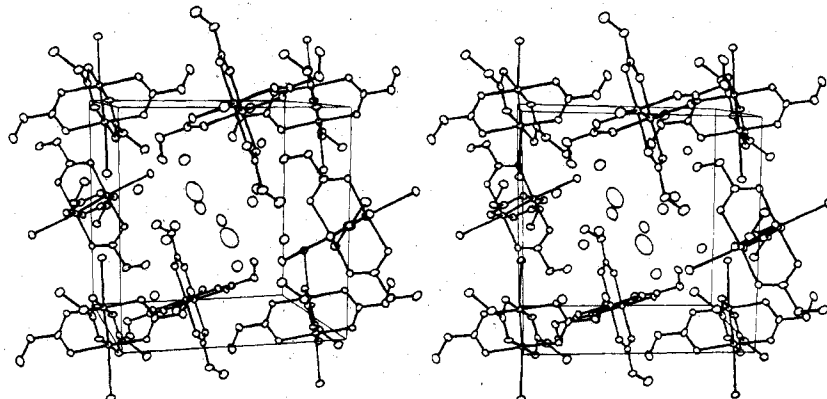


Figure 3. An ORTEP stereoview of the unit cell of 2.

**Table V.** Bond Distances and Bond Angles for Triclinic  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 2^{2/3}\text{H}_2\text{O}$  (2)

Bond Distances and Bond Angles for Molecule I				Bond Angles, Deg			
Bond Distances, Å				Bond Distances and Bond Angles for Molecule III			
Mo(1)-Mo(1)'	2.107 (1)			Mo(3)-Mo(3)'	2.103 (1)		
-Cl(1)	2.907 (1)			-Cl(3)	2.829 (2)		
-O(11)'	2.112 (4)			-O(31)'	2.147 (4)		
-O(12)	2.130 (4)			-O(32)	2.102 (4)		
-O(13)	2.116 (5)			-O(33)	2.133 (4)		
-O(14)'	2.115 (5)			-O(34)'	2.129 (4)		
O(11)-C(11)	1.273 (8)	O(13)-C(13)	1.236 (9)	O(31)-C(31)	1.269 (8)	O(33)-C(33)	1.259 (8)
O(12)-C(11)	1.266 (8)	O(14)-C(13)	1.315 (9)	O(32)-C(31)	1.259 (8)	O(34)-C(33)	1.282 (8)
C(11)-C(12)	1.498 (9)	C(13)-C(14)	1.50 (1)	C(31)-C(32)	1.541 (9)	C(33)-C(34)	1.50 (1)
C(12)-N(11)	1.50 (1)	C(14)-N(12)	1.45 (1)	C(32)-N(31)	1.45 (1)	C(34)-N(32)	1.51 (1)
Bond Angles, Deg				Bond Angles, Deg			
Mo(1)'-Mo(1)-Cl(1)	166.90 (5)	Mo(1)'-O(11)-C(11)	116.9 (4)	Mo(2)'-Mo(2)-Cl(2)	168.04 (5)	Mo(2)'-O(21)-C(21)	117.1 (4)
-O(11)'	91.5 (1)	Mo(1)-O(12)-C(11)	115.6 (4)	-O(21)'	90.7 (1)	Mo(2)-O(22)-C(21)	116.0 (4)
-O(12)	92.1 (1)	O(11)-C(11)-O(12)	123.8 (6)	-O(22)	92.6 (1)	O(21)-C(21)-O(22)	123.5 (6)
-O(13)	90.6 (1)	-C(12)	117.6 (6)	-O(23)	93.0 (1)	-C(22)	116.1 (6)
-O(14)'	93.0 (1)	O(12)-C(11)-C(12)	118.6 (6)	-O(24)'	90.3 (1)	O(22)-C(21)-C(22)	120.3 (6)
O(11)'-Mo(1)-O(12)	176.3 (2)	C(11)-C(12)-N(11)	109.1 (6)	O(21)'-Mo(2)-O(22)	176.7 (2)	C(21)-C(22)-N(21)	109.3 (5)
-O(13)	90.8 (2)	Mo(1)-O(13)-C(13)	118.7 (4)	-O(23)	90.6 (2)	Mo(2)-O(23)-C(23)	115.4 (4)
-O(14)'	89.9 (2)	Mo(1)'-O(14)-C(13)	114.6 (4)	-O(24)'	89.2 (2)	Mo(2)'-O(24)-C(23)	117.1 (4)
O(12)-Mo(1)-O(13)	89.9 (2)	O(13)-C(13)-O(14)	122.9 (6)	O(22)-Mo(2)-O(23)	89.4 (2)	O(23)-C(23)-O(24)	124.0 (6)
-O(14)'	89.1 (2)	-C(14)	116.4 (7)	-O(24)'	90.6 (2)	-C(24)	120.8 (6)
O(13)-Mo(1)-O(14)'	176.3 (2)	O(14)-C(13)-C(14)	120.6 (7)	O(23)-Mo(2)-O(24)'	176.6 (2)	O(24)-C(23)-C(24)	115.2 (6)
		C(13)-C(14)-N(12)	112.9 (7)			C(23)-C(24)-N(22)	111.5 (5)

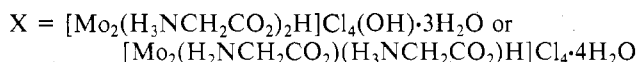
**Table VI.** Some Average Bond Lengths (Å) and Angles (deg)<sup>a</sup>

Mo-Mo	2.108 ± 0.003		
Mo-Mo-O	91.7 ± 0.8		
Mo-O	2.122 ± 0.010	Mo-Cl	2.872 ± 0.023
C-O	1.267 ± 0.012	C-C	1.52 ± 0.015
C-N	1.48 ± 0.024		

<sup>a</sup> The intervals are the mean deviations from the mean.

ence(s) between the two preparative procedures may be the crucial one(s). The procedure giving the monoclinic form, **1**, is the simplest and more obvious, but the series of steps involved in preparing **2** is chemically much more interesting and puzzling.

Up to a point the chemistry preceding the formation of crystalline **2** has been clarified already by Bino and Ardon.<sup>3</sup> They showed that in the first step the bridging hydride ligand is retained, while glycol groups replace ligated  $\text{Cl}^-$  ions, suggested one of the following processes for formation of the purple species, and showed that the process is readily reversible without isotopic exchange of the hydride ligand.



Bino and Ardon had shown that when the carboxylic acid used is acetic acid, the yellow product ultimately formed

without evolution of hydrogen gas is  $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ . This present work shows conclusively that an analogous process in the glycine system occurs in which X loses the H as  $\text{H}^+$  (certainly not as  $1/2\text{H}_2$ ) so that the molybdenum finally appears as  $\text{Mo}^{\text{II}}$  in  $\text{Mo}_2(\text{gly})_4\text{Cl}_4 \cdot 2.67\text{H}_2\text{O}$ .

The remaining mystery in this fascinating system is the exact nature of the violet, H-containing intermediate compound X. We shall continue to try to identify this substance fully.

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**Registry No.** **1**, 69881-47-6; **2**, 69881-48-7;  $\text{K}_4\text{Mo}_2\text{Cl}_8$ , 25448-39-9;  $\text{Cs}_3\text{Mo}_2\text{Cl}_8\text{H}$ , 57719-40-1.

**Supplementary Material Available:** Tables of observed and calculated structure factors for both compounds (21 pages). Ordering information is given on any current masthead page.

## References and Notes

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- (7) See, for example: Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.*, **1979**, *18*, 1143.
- (8) All crystallographic computations were performed on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas, using the Enraf-Nonius software with certain local modifications.