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Complexes of Dimolybdenum(II) with DL-Amino Acids. 2. Crystal Structure of Compounds Containing DL-Valine and DL-Leucine

FRANCOISE APFELBAUM and AVI BINO*

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

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Abstract

$[Mo_2(D\text{-}Val)_2(L\text{-}Val)_2](ZnCl_4)_2\cdot 4H_2O$ (**1**) and $[Mo_2(D\text{-}Leu)_2(L\text{-}Leu)_2](PTS)_2Cl_2\cdot 2H_2O$ (**2**) (Val = Valine; Leu = Leucine; PTS = *p*-toluensulfonate) were prepared by reacting Mo_2^{4+} with the racemic amino acid in water followed by the addition of the appropriate counter ion. $[Mo_2(D\text{-}Val)(L\text{-}Val)(NCS)_4]\cdot 1\frac{1}{2}H_2O$ (**3**) was prepared by adding NCS^- ions to a solution of Mo_2^{4+} and DL-Valine. The structures of **1**, **2** and **3** were determined by X-ray crystallography. Compound **1** is triclinic, space group $P\bar{1}$ with $a = 12.162(1)$, $b = 12.780(1)$, $c = 7.429(1)$ Å, $\alpha = 106.52(2)$, $\beta = 92.61(3)$, $\gamma = 72.89(3)°$, $V = 1057(1)$ Å^3 and $Z = 1$. Compound **2** is triclinic, space group $P\bar{1}$ with $a = 9.326(1)$, $b = 15.546(2)$, $c = 9.092(1)$ Å, $\alpha = 92.41(3)$, $\beta = 100.27(2)$, $\gamma = 76.87(2)°$, $V = 1263(1)$ Å^3 and $Z = 1$. Compound **3** is triclinic, space group $P\bar{1}$ with $a = 12.221(1)$, $b = 13.366(2)$, $c = 9.745(1)$ Å, $\alpha = 104.39(2)$, $\beta = 103.50(3)$, $\gamma = 71.05(3)°$, $V = 1438(1)$ Å^3 and $Z = 2$. In **1** and **2** the dimeric unit resides on a crystallographic center of symmetry and the four ligands are coordinated to the Mo_2^{4+} unit in the cyclic order of DDLL. In **3**, the molecule has a cisoid arrangement of the amino acid ligands and the four NCS^- ligands.

Introduction

Recently, we reported the structure of crystalline compounds obtained by the reaction of the quadruply-bonded dimolybdenum(II) ion, Mo_2^{4+} with several racemic amino acids [1]. Theoretically, this reaction may yield in solution the following six isomers: Mo_2D_4, Mo_2D_3L, Mo_2DDLL, Mo_2DLDL, Mo_2L_3D and Mo_2L_4 in the ratio 1:4:4:2:4:1, respectively. However, in solids obtained from the reaction mixtures, only one isomer was isolated almost quantitatively, namely Mo_2DDLL. The DL-amino acids that have been examined are phenylalanine (Phe), tyrosine (Tyr) and C-phenylglycine (phGly) and the isomer appearing in all three compounds is $[Mo_2(D\text{-}O_2CCH(NH_3)R)_2(L\text{-}O_2CCH(NH_3)R)_2]^{4+}$ when $R = CH_2C_6H_5$, $CH_2CH_6H_4OH$ and C_6H_5, respectively. The zwitterionic amino acids in these compounds are coordinated to the Mo_2^{4+} unit through the carboxyl oxygen atoms in the cyclic order of DDLL. The use of different counter ions for the precipitation of the various complexes, iodide for Phe and Tyr, and *p*-toluensulfonate (PTS) for phGly, did not affect the isomer distribution in the solid state.

This work is part of a project in which we continue to study the factors governing the stereochemistry of this system by introducing additional parameters. In some cases, isomer distribution is affected by intramolecular steric interaction, namely, the interaction between the chiral amino acids in the complex. Here, we examine the influence of the R residues of the amino acids by substituting the relatively bulky aromatic R groups with aliphatic chains. We have reacted Mo_2^{4+} with DL-Valine and DL-Leucine and structurally characterized two new dimolybdenum(II) compounds derived from these reactions. Both compounds exhibit the same steric arrangement of the four bridging amino acid ligands about the Mo_2^{4+} unit, *i.e.* they are coordinated in the cyclic order of DDLL.

It was previously shown that the yellow solution of $[Mo_2A_4]^{4+}$, when A is an amino acid, reacts with NCS^- ions and a red–purple, mixed isothiocyanato–amino acid compound $[Mo_2A_2(NCS)_4]$ is formed [2]. In order to examine the products of the reaction of NCS^- with the racemic amino acid–Mo_2^{4+} complexes we prepared the corresponding mixed ligand compound with A = DL-valine and analyzed its structure. The following compounds were prepared and characterized by X-ray techniques: $[Mo_2(D\text{-}Val)_2(L\text{-}Val)_2](ZnCl_4)_2\cdot 4H_2O$ (**1**), $[Mo_2(D\text{-}Leu)_2(L\text{-}Leu)_2](PTS)_2Cl_2\cdot 2H_2O$ (**2**) and $[Mo_2(D\text{-}Val)(L\text{-}Val)(NCS)_4]\cdot 1\frac{1}{2}H_2O$ (**3**).

Experimental

Preparation of $[Mo_2(D\text{-}Val)_2(L\text{-}Val)_2](ZnCl_4)_2\cdot 4H_2O$ (1)

$K_4Mo_2Cl_8$ (0.05 g), prepared by a literature method [3], was dissolved in 10 ml of 0.05 M DL-

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*Author to whom correspondence should be addressed.

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TABLE 1. Crystallographic Data

Compound	1	2	3
Formula	$Mo_2Zn_2Cl_8O_{12}N_4C_{20}H_{52}$	$Mo_2Cl_2S_2O_{16}N_4C_{38}H_{70}$	$Mo_2S_4O_{5.5}N_6C_{14}H_{23}$
Molecular weight	1146.89	1165.90	683.51
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.162(1)	9.326(1)	12.221(1)
b (Å)	12.780(1)	15.546(2)	13.366(2)
c (Å)	7.429(1)	9.092(1)	9.745(1)
α (°)	106.52(2)	92.41(3)	104.39(2)
β (°)	92.61(3)	100.27(2)	103.50(3)
γ (°)	72.89(3)	76.87(2)	71.05(3)
V (Å^3)	1057(1)	1263(1)	1438(1)
Z	1	1	2
D_{calc} (g cm^{-3})	1.801	1.533	1.579
μ (cm^{-1})	21.29	6.69	10.84
Range of 2θ (°)	3–45	4–45	4–45
No. unique data	2733	3253	3706
Data with $F_o^2 > 3\sigma(F_o^2)$	2259	2704	2889
R	0.068	0.057	0.074
R_w	0.079	0.062	0.083

Valine and 0.1 M HCl. A few grains of $ZnCl_2$ were added and the solution was slowly evaporated under a stream of argon. Yellow crystals were obtained after 24 h.

Preparation of [Mo_2(D-Leu)$_2$(L-Leu)$_2$](PTS)$_2Cl_2\cdot 2H_2O$ (2)

$K_4Mo_2Cl_8$ (0.05 g) was dissolved in 10 ml of saturated solution of DL-Leucine in HCl 0.1 M. The yellow solution was allowed to mix by diffusion through a glass frit with a 1 M solution of *p*-toluenesulfonic acid (HPTS) at 20 °C. Yellow crystals were deposited after 24 h.

Preparation of [Mo_2(D-Val)(L-Val)(NCS)$_4$]$\cdot 1\frac{1}{2}H_2O$ (3)

$K_4Mo_2Cl_8$ (0.05 g) was dissolved in 10 ml of 0.05 M of DL-Valine and 0.1 M HCl. The solution was allowed to mix by diffusion through a glass frit with a 1 M solution of KCNS at 20 °C. Red–purple crystals were formed over a period of 24 h.

X-ray Crystallography

Data were collected on a PW1100 Phillips diffractometer. Mo Kα ($\lambda = 0.71069$ 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 25 reflections in the range of $12° < \theta < 16°$. Data were measured by using a ω–2θ motion. Crystallographic data and other pertinent information are given in Table 1. For each crystal, Lorentz and polarization corrections were applied. No absorption correction was applied. The heavy-atom positions in **1**–**3** were obtained from a three-dimensional Patterson function.

In **1**, anisotropic thermal parameters were used for all atoms except for the carbon atoms and the water oxygen atom. In **2**, anisotropic thermal parameters were used for all atoms except for the PTS carbon atoms and for the water oxygen atom and in **3** for the molybdenum, sulfur oxygen, nitrogen and the chiral carbon atoms.*

The discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table 1. See also 'Supplementary Material'.

Powder Diffraction

X-ray diffraction data were recorded using a Philips Powder diffractometer with Ni-filtered Cu Kα_1 radiation ($\lambda = 1.5405$ Å). The calculated pattern of **3** was obtained by using the Program for Calculating X-ray Powder Diffraction Patterns, Version 5 [4].

Results and Discussion

The atomic positional parameters of structures 1–3 are listed in Tables 2, 4 and 6 and Tables 3, 5, and 7 present the important bond lengths and angles of **1**–**3**, respectively. The structures and numbering schemes of the dimeric complexes are shown in Figs. 1–3. In compounds **1** and **2** there is a crystallographic inversion center midway between the molybdenum atoms of the dimer. Therefore, there is only half a $[Mo_2(O_2CCH(NH_3^+)R)_4]^{4+}$ unit in the asym-

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*All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE 2. Positional Parameters for **1**[a]

Atom	x	y	z
Mo	0.0371(1)	−0.0216(1)	0.1202(1)
Zn	0.4843(1)	0.2078(1)	0.5686(2)
Cl(1)	0.5599(3)	0.1394(3)	0.8116(5)
Cl(2)	0.4910(4)	0.3923(3)	0.6261(6)
Cl(3)	0.6016(3)	0.1129(3)	0.3018(5)
Cl(4)	0.3042(4)	0.2014(5)	0.5078(6)
O(1)	0.1523(8)	−0.1744(7)	−0.048(1)
O(2)	−0.0758(8)	0.1270(7)	0.302(1)
O(3)	0.1629(7)	0.0627(7)	0.113(1)
O(4)	−0.0840(7)	−0.1074(8)	0.142(1)
OW(1)	0.174(1)	−0.080(1)	0.374(2)
N(1)	0.338(1)	−0.332(1)	−0.245(2)
N(2)	0.3533(9)	0.1117(9)	0.064(2)
C(1)	0.149(1)	−0.193(1)	−0.226(2)
C(2)	0.234(1)	−0.297(1)	−0.352(2)
C(3)	0.185(1)	−0.397(1)	−0.439(2)
C(4)	0.144(2)	−0.440(2)	−0.282(3)
C(5)	0.088(2)	−0.367(2)	−0.565(3)
C(6)	0.159(1)	0.109(1)	−0.020(2)
C(7)	0.250(1)	0.167(1)	−0.029(2)
C(8)	0.207(1)	0.295(1)	0.069(2)
C(9)	0.111(1)	0.352(1)	−0.045(2)
C(10)	0.304(1)	0.351(1)	0.091(2)
OW(2)	−0.295(1)	0.350(1)	−0.113(2)

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

TABLE 3. Important Bond Lengths (Å) and Angles (°) for **1**

Mo–Mo′	2.104(1)	C(2)–N(1)	1.49(1)
Mo–O(1)	2.122(7)	C(2)–C(1)	1.51(1)
Mo–O(2)	2.119(7)	C(2)–C(3)	1.53(2)
Mo–O(3)	2.12(1)	C(7)–N(2)	1.50(1)
Mo–O(4)	2.11(1)	C(7)–C(6)	1.51(2)
Mo–OW(1)	2.58(1)	C(7)–C(8)	1.52(1)

Mo′–Mo–O(1)	91.2(2)	O(2)–Mo–OW(1)	96.8(5)
Mo′–Mo–O(2)	92.0(2)	O(3)–Mo–O(4)	176.6(3)
Mo′–Mo–O(3)	90.7(2)	O(3)–Mo–OW(1)	78.1(4)
Mo′–Mo–O(4)	92.8(2)	O(4)–Mo–OW(1)	98.6(4)
Mo′–Mo–OW(1)	166.0(3)	N(1)–C(2)–C(1)	109(1)
O(1)–Mo–O(2)	176.7(3)	N(1)–C(2)–C(3)	111(1)
O(1)–Mo–O(3)	88.5(4)	C(1)–C(2)–C(3)	115(1)
O(1)–Mo–O(4)	91.6(4)	N(2)–C(7)–C(6)	107(1)
O(1)–Mo–OW(1)	80.3(5)	N(2)–C(7)–C(8)	111(1)
O(2)–Mo–O(3)	92.4(4)	C(6)–C(7)–C(8)	111(1)
O(2)–Mo–O(4)	87.3(4)		

metric unit, with the other half related to it by the crystallographic inversion center.

From Figs. 1 and 2 it can be seen that in both **1** and **2** the isomer is Mo_2DDLL as has been previously found in the aromatic amino acid complexes [1]. In **1**, there are water oxygen atoms bonded to the molybdenum atoms in the axial positions with

TABLE 4. Positional Parameters for **2**[a]

Atom	x	y	z
Mo	0.45953(9)	0.45588(5)	0.55860(8)
Cl	0.3862(3)	0.3098(2)	0.6935(3)
S	1.0099(3)	0.3497(2)	0.1780(3)
O(1)	0.2336(6)	0.5132(4)	0.4639(6)
O(2)	0.6803(7)	0.3966(4)	0.6645(7)
O(3)	0.4712(7)	0.3654(4)	0.3759(6)
O(4)	0.4453(7)	0.5414(4)	0.7472(6)
O(10)	0.8684(8)	0.3452(5)	0.0867(8)
O(11)	0.9946(9)	0.3962(4)	0.3164(8)
O(12)	1.101(1)	0.3861(5)	0.097(1)
N(1)	−0.0534(9)	0.5838(5)	0.361(1)
N(2)	0.5469(9)	0.3644(5)	−0.0019(8)
C(1)	0.214(1)	0.5749(6)	0.370(1)
C(2)	0.056(1)	0.6121(7)	0.286(1)
C(3)	0.020(1)	0.7099(7)	0.248(1)
C(4)	−0.004(1)	0.7741(8)	0.377(1)
C(5)	−0.061(2)	0.8686(9)	0.310(2)
C(6)	0.139(2)	0.7711(9)	0.494(1)
C(7)	0.513(1)	0.3875(6)	0.261(1)
C(8)	0.507(1)	0.3232(6)	0.130(1)
C(9)	0.598(1)	0.2337(7)	0.172(1)
C(10)	0.587(1)	0.1635(7)	0.047(1)
C(11)	0.694(2)	0.0773(9)	0.117(2)
C(12)	0.433(2)	0.1461(9)	−0.008(1)
C(100)	1.104(1)	0.2391(6)	0.223(1)
C(101)	1.050(1)	0.1711(7)	0.149(1)
C(102)	1.124(1)	0.0835(8)	0.190(1)
C(103)	1.248(1)	0.0676(8)	0.303(1)
C(104)	1.301(1)	0.1385(7)	0.378(1)
C(105)	1.228(1)	0.2256(6)	0.337(1)
C(106)	1.327(2)	−0.029(1)	0.349(2)
OW	0.265(1)	0.4771(6)	0.980(1)

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

TABLE 5. Important Bond Lengths (Å) and Angles (°) for **2**

Mo–Mo′	2.114(1)	C(2)–N(1)	1.47(1)
Mo–Cl	2.892(2)	C(2)–C(1)	1.53(1)
Mo–O(1)	2.132(5)	C(2)–C(3)	1.52(1)
Mo–O(2)	2.130(5)	C(8)–N(2)	1.52(1)
Mo–O(3)	2.131(5)	C(8)–C(7)	1.53(1)
Mo–O(4)	2.127(5)	C(8)–C(9)	1.48(1)

Mo′–Mo–Cl	169.34(7)	O(1)–Mo–O(4)	90.9(2)
Mo′–Mo–O(1)	91.9(1)	O(2)–Mo–O(3)	92.2(3)
Mo′–Mo–O(2)	91.1(2)	O(2)–Mo–O(4)	87.4(3)
Mo′–Mo–O(3)	90.1(1)	O(3)–Mo–O(4)	177.2(2)
Mo′–Mo–O(4)	92.7(1)	N(1)–C(2)–C(1)	109.6(9)
Cl–Mo–O(1)	94.3(2)	N(1)–C(2)–C(3)	115.3(9)
Cl–Mo–O(2)	83.0(2)	C(1)–C(2)–C(3)	115.4(8)
Cl–Mo–O(3)	81.3(1)	N(2)–C(8)–C(7)	108.3(7)
Cl–Mo–O(4)	95.9(2)	N(2)–C(8)–C(9)	115.0(9)
O(1)–Mo–O(2)	176.6(2)	C(7)–C(8)–C(9)	112.1(9)
O(1)–Mo–O(3)	89.4(2)		

TABLE 6. Positional Parameters for 3[a]

Atom	x	y	z
Mo(1)	0.34856(8)	0.10166(7)	0.07380(9)
Mo(2)	0.16591(8)	0.11816(7)	−0.0033(1)
S(1)	0.3108(6)	0.4120(3)	0.4671(5)
S(2)	0.0825(4)	−0.1496(4)	0.1862(6)
S(3)	−0.0363(6)	0.3762(6)	0.3663(5)
S(4)	0.4772(5)	−0.1603(5)	0.3879(6)
O(1)	0.3507(7)	0.2059(6)	−0.0558(8)
O(2)	0.1604(7)	0.2242(6)	−0.1338(6)
O(3)	0.3958(7)	−0.0337(6)	−0.0927(8)
O(4)	0.2072(7)	−0.0128(7)	−0.1743(9)
N(1)	0.3463(9)	0.2310(7)	0.252(1)
N(2)	0.1323(9)	0.0101(9)	0.097(1)
N(3)	0.0852(9)	0.2443(9)	0.148(1)
N(4)	0.3935(8)	−0.0069(8)	0.2119(9)
N(5)	0.153(1)	0.329(1)	−0.339(1)
N(6)	0.247(2)	−0.178(2)	−0.389(3)
C(1)	0.253(1)	0.2465(9)	−0.130(1)
C(2)	0.253(1)	0.324(1)	−0.221(1)
C(3)	0.250(1)	0.440(1)	−0.125(2)
C(4)	0.150(2)	0.484(2)	−0.034(2)
C(5)	0.361(2)	0.443(2)	−0.017(2)
C(6)	0.314(1)	−0.064(1)	−0.177(1)
C(7)	0.348(1)	−0.170(1)	−0.283(2)
C(8)	0.388(2)	−0.265(2)	−0.183(2)
C(9)	0.310(2)	−0.254(2)	−0.075(3)
C(10)	0.404(2)	−0.375(2)	−0.308(3)
C(11)	0.039(1)	0.301(1)	0.239(2)
C(12)	0.330(1)	0.305(1)	0.337(2)
C(13)	0.425(1)	−0.068(1)	0.280(2)
C(14)	0.113(1)	−0.055(1)	0.136(1)
OW(1)	0.086(2)	0.611(2)	0.302(2)
OW(2)	0.236(2)	0.122(2)	0.490(3)
OW(3)	0.690(3)	0.330(2)	0.640(3)

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

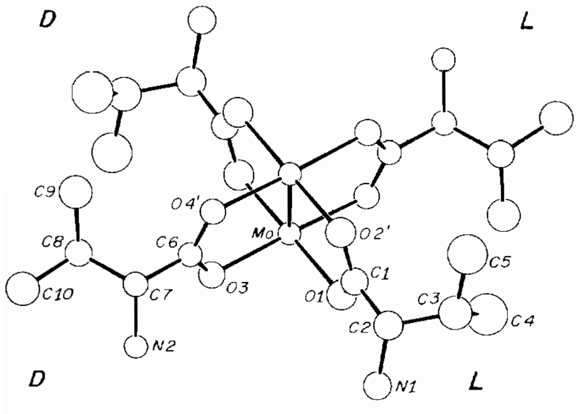

Fig. 1. The structure of $[Mo_2(D\text{-}Val)_2(L\text{-}Val)_2]^{4+}$ as found in 1.

Mo–O(OH_2) distance of 2.58(1) Å. The two tetrahedral $ZnCl_4^{2-}$ anions in the cell are hydrogen bonded to the lattice water oxygen atoms with Cl–OW distances in the range of 3.18(1)–3.51(1) Å and to NH_3^+ nitrogen atoms with Cl–N distances in the range 3.18(1)–3.45(1) Å. In 2, the axial positions are occupied by two chloride ions, weakly bonded to the molybdenum atoms with a Mo–Cl distance of 2.892(2) Å. The axial interactions are different from those found in the chiral isomer $[Mo_2(L\text{-}Leu)_4]^{4+}$ in which the dimetal unit is bonded to one Cl^- ion on one side and to a PTS oxygen atom on the other side [5].

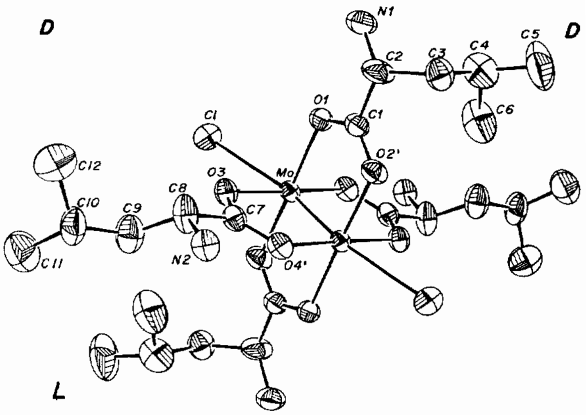

Fig. 2. The structure of $[Mo_2(D\text{-}Leu)_2(L\text{-}Leu)_2]^{4+}$ as found in 2.

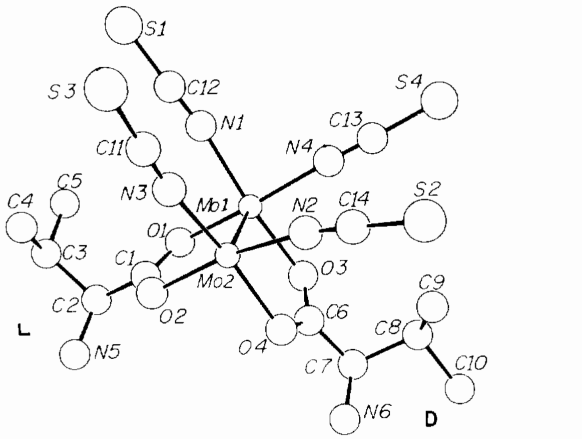

Fig. 3. The structure of $[Mo_2(D\text{-}Val)(L\text{-}Val)(NCS)_4]$ as found in 3.

The two PTS anions in the cell are involved in a hydrogen bonding network with (O_2S)O–O distances of 2.67(1)–2.80(1) Å and (O_2S)O–NH_3^+ distances of 2.87(1)–2.91(1) Å.

The four NH_3^+ groups in **1** and **2** form an intramolecular hydrogen bond to the carboxylate oxygen atoms in a 'right, right, left, left' geometry [1]. In this arrangement, one pair of neighbouring amino acids, D and L, forms hydrogen bonds to oxygen atoms, coordinated to the same metal atom, while the other pair is hydrogen bonded to oxygen atoms coordinated to the other metal atom.

TABLE 7. Important Bond Lengths (Å) and Angles (°) for 3

Mo(1)–Mo(2)	2.139(1)	Mo(2)–N(3)	2.089(9)
Mo(1)–O(1)	2.110(9)	C(2)–N(5)	1.47(1)
Mo(1)–O(3)	2.130(6)	C(2)–C(1)	1.52(2)
Mo(1)–N(1)	2.123(8)	C(2)–C(3)	1.60(1)
Mo(1)–N(4)	2.08(1)	C(7)–N(6)	1.42(2)
Mo(2)–O(2)	2.104(9)	C(7)–C(6)	1.53(2)
Mo(2)–O(4)	2.113(7)	C(7)–C(8)	1.66(3)
Mo(2)–N(2)	2.12(1)		
Mo(2)–Mo(1)–O(1)	91.7(3)	Mo(1)–Mo(2)–N(3)	102.9(3)
Mo(2)–Mo(1)–O(3)	91.4(2)	O(2)–Mo(2)–O(4)	89.6(3)
Mo(2)–Mo(1)–N(1)	102.6(3)	O(2)–Mo(2)–N(2)	166.3(4)
Mo(2)–Mo(1)–N(4)	103.2(3)	O(2)–Mo(2)–N(3)	92.2(4)
O(1)–Mo(1)–O(3)	90.5(3)	O(4)–Mo(2)–N(2)	86.9(4)
O(1)–Mo(1)–N(1)	88.3(3)	O(4)–Mo(2)–N(3)	166.5(4)
O(1)–Mo(1)–N(4)	165.0(4)	N(2)–Mo(2)–N(3)	88.2(5)
O(3)–Mo(1)–N(1)	166.0(4)	N(5)–C(2)–C(1)	109(1)
O(3)–Mo(1)–N(4)	87.3(4)	N(5)–C(2)–C(3)	112(1)
N(1)–Mo(1)–N(4)	90.3(4)	C(1)–C(2)–C(3)	111(1)
Mo(1)–Mo(2)–O(2)	90.6(3)	N(6)–C(7)–C(6)	108(2)
Mo(1)–Mo(2)–O(4)	90.4(3)	N(6)–C(7)–C(8)	112(2)
Mo(1)–Mo(2)–N(2)	102.7(4)	C(6)–C(7)–C(8)	104(2)

In compound 3 there are two molecules in the cell of space group $P\bar{1}$ and no crystallographic symmetry is imposed upon the dimeric complex. The structure of this mixed amino acid–isothiocyanato complex is similar to that found for $[Mo_2(Gly)_2(NCS)_4]\cdot H_2O$ and for the chiral $[Mo_2(L\text{-isoleu})_2(NCS)_4]\cdot 4.5H_2O$ [2]. The Mo–Mo distance of 2.139(1) Å in 3 is slightly longer than that in $[Mo_2(Gly)_4]^{4+}$, 2.115(1)–2.103(1) Å [6] and shorter than the value in $[Mo_2(NCS)_8]^{4-}$ which is in the range of 2.162(1)–2.177(1) Å [7]. The two intramolecular NH_3^+–O(carboxylate) hydrogen bonds in 3 (one in D and one in L) point to the same direction, preserving the geometry found for the complete DDLL isomer as in 1.

The results presented here demonstrate once again the preferential crystallization of only one isomer, namely Mo_2DDLL. Substitution of the bulky aromatic amino acids, such as phenylalanine, tyrosine or phenylglycine with aliphatic ones did not alter the isomer distribution in the solid state. This can be ascribed to a low solubility of salts of this centrosymmetric isomer regardless of the nature of the amino acid ligands, or to its predominance in solution. The structure and geometry of these Mo_2LLDD^{4+} complexes do not offer an obvious explanation to an extensive deviation from the theoretical statistical isomer distribution in solution.

The reaction of NCS^- with Mo_2LLDD^{4+} or with a mixture of all possible isomers may yield chiral $Mo_2D_2(NCS)_4$ and non-chiral $Mo_2DL(NCS)_4$. The powder diffraction pattern of the solid, obtained by addition of NCS^- to a solution of Mo_2^{4+} + DL-valine was found to be identical with the simulated pattern of 3. The diffraction pattern of $Mo_2(L\text{-Val})_2(NCS)_4$, which is produced by using L-Valine instead of DL-Valine differs from that of 3. This indicates that only one isomer crystallizes under the above conditions, compound 3, and that no chiral complexes are present in the solid.

Supplementary Material

Tables of observed and calculated structure factors, thermal parameters and non-essential bond distances and angles for **1**, **2** and **3** (54 pages) are available from the authors on request.

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