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Complexes of Dimolybdenum(II) with DL-Amino Acids

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$[Mo_2(D\text{-phe})_2(L\text{-phe})_2]I_4 \cdot 6H_2O$ (**1**), $[Mo_2(D\text{-tyr})_2(L\text{-tyr})_2]I_4 \cdot 6H_2O$ (**2**), and $[Mo_2(D\text{-}C\text{-phgly})_2(L\text{-}C\text{-phgly})_2](PTS)_4 \cdot 4H_2O$ (**3**) were obtained by the reaction of Mo_2^{4+} with the appropriate DL-amino acid in aqueous solution, followed by the addition of counterions. The structures of **1–3** were determined by X-ray crystallography. **1** is triclinic, space group $P\bar{1}$, with a = 11.969 (1) Å, b = 13.746 (2) Å, c = 9.457 (1) Å, α = 104.90 (2)°, β = 107.49 (3)°, γ = 66.47 (2)°, V = 1344 (1) Å^3, and Z = 1. **2** is triclinic, space group $P\bar{1}$, with a = 12.666 (1) Å, b = 12.952 (1) Å, c = 8.918 (1) Å, α = 98.50 (3)°, β = 92.31 (2)°, γ = 63.58 (2)°, V = 1254 (1) Å^3, and Z = 1. **3** is triclinic, space group $P\bar{1}$, with a = 11.361 (1) Å, b = 16.538 (2) Å, c = 10.110 (1) Å, α = 95.44 (2)°, β = 110.84 (2)°, γ = 75.68 (2)°, V = 1720 (1) Å^3, and Z = 1. The dimeric molecules in the three structures reside on a crystallographic inversion center, and the four chiral ligands are arranged around the Mo–Mo unit in the cyclic order of DDLL.

Introduction

Several compounds containing chiral amino acids and other carboxylic acids coordinated to the Mo_2^{4+} unit have been prepared recently. The structures of three compounds, $[Mo_2(L\text{-leu})_4]Cl_2(PTS)_2 \cdot 2H_2O$ (PTS = $CH_3C_6H_4SO_3^-$),[1] $[Mo_2(L\text{-isoleu})_2(NCS)_4] \cdot 4^1/_2H_2O$,[2] and $[Mo_2(D\text{-mandelato})_4] \cdot 2THF$,[3] were determined by X-ray crystallography. In the first two complexes the amino acids are zwitterions, coordinated to the dimolybdenum unit through the two oxygen atoms of the carboxyl end. All these complexes were prepared by reacting the aquated Mo_2^{4+} ion with the appropriate chiral amino or other carboxylic acid (D or L). This work deals with the stereochemistry and structure of the crystalline compounds obtained by the reaction of Mo_2^{4+} with *racemic* amino acids.

We have reacted DL-phenylalanine, DL-tyrosine, and DL-*C*-phenylglycine (DL-*C*-phgly) with Mo_2^{4+} in aqueous solutions, crystallized the various products, and structurally characterized the new compounds by X-ray techniques. All three compounds have the same steric arrangement of the four amino acid ligands: the chiral bridging ligands are coordinated to the Mo_2^{4+} in the cyclic order of DDLL. These products are obtained in yields higher than 90%.

The preparation and structures of $[Mo_2(D\text{-phe})_2(L\text{-phe})_2]I_4 \cdot 6H_2O$ (**1**), $[Mo_2(D\text{-tyr})_2(L\text{-tyr})_2]I_4 \cdot 6H_2O$ (**2**), and $[Mo_2(D\text{-}C\text{-phgly})_2(L\text{-}C\text{-phgly})_2](PTS)_4 \cdot 4H_2O$ (**3**) are described.

Experimental Section

Preparations. The starting material for all compounds is $K_4Mo_2Cl_8$, prepared by a literature method.[4] The different products were obtained when 50-mg samples were dissolved in 10 mL of 0.05 M of the corresponding DL-amino acid and 0.1 M HCl. The resulting yellow solutions were allowed to mix by diffusion through a glass frit at 20 °C with a solution containing the appropriate counterion. All manipulations were carried out under an atmosphere of oxygen-free argon.

$[Mo_2(D\text{-phe})_2(L\text{-phe})_2]I_4 \cdot 6H_2O$ (1) and $[Mo_2(D\text{-tyr})_2(L\text{-tyr})_2]I_4 \cdot 6H_2O$ (2). A solution of 1 M KI was used for the crystallization of **1** and **2**. In both cases yellow crystals were obtained after ca. 24 h in yields >90%.

$[Mo_2(D\text{-}C\text{-phgly})_2(L\text{-}C\text{-phgly})_2](CH_3C_6H_4SO_3)_4 \cdot 4H_2O$ (3). The yellow solution of the complex was mixed with a solution of 1 M *p*-toluenesulfonic acid. Yellow crystals were obtained after ca. 24 h in >90% yield.

Table I. Crystallographic Data

compd no.	**1**	**2**	3
formula	$Mo_2I_4O_{14}N_4$-$C_{36}H_{56}$	$Mo_2I_4O_{18}N_4$-$C_{36}H_{56}$	$Mo_2S_4O_{24}N_4$-$C_{60}H_{72}$
fw	1468.35	1532.76	1553.37
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	11.969 (1)	12.266 (1)	11.361 (1)
b, Å	13.746 (2)	12.952 (1)	16.538 (2)
c, Å	9.457 (1)	8.918 (1)	10.110 (1)
α, deg	104.90 (2)	98.50 (3)	95.44 (2)
β, deg	107.49 (3)	92.31 (2)	110.84 (2)
γ, deg	66.47 (2)	63.58 (2)	75.68 (2)
V, Å^3	1344 (1)	1254 (1)	1720 (1)
d(calcd), g cm^{-3}	1.814	2.028	1.499
Z	1	1	1
cryst size, mm	0.2 × 0.2 × 0.3	0.1 × 0.2 × 0.3	0.3 × 0.3 × 0.4
μ, cm^{-1}	26.13	28.07	4.93
range of 2θ, deg	3–46	3–45	3–45
no. of unique data	3683	3263	4452
no. of data with $F_o^2 > 3\sigma(F_o^2)$	2661	2822	3765
R_1	0.053	0.039	0.065
R_2	0.059	0.042	0.069

X-ray Crystallography. Data were collected on a Philips PW1100 four-circle computer-controlled diffractometer. Mo Kα (λ = 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 $12° < \theta < 16°$.[5,6] Data were measured by using a ω-2θ motion. The scan width, $\Delta\omega$, for each reflection was 1° with a scan time of 20 s. Background measurements were made at both limits of each scan. Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. Intensity data were corrected for absorption only for **2** by the empirical ψ-scan method. ψ scans at χ = 90° for several reflections of **1** showed no variation greater than 9%. 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 oxygen atoms of the uncoordinated water molecules. In **2**, anisotropic thermal parameters were used for all atoms; in **3**, they were used only for the molybdenum, sulfur, coordinated oxygen, and nitrogen atoms, and isotropic ones were used for the rest of the atoms.

The discrepancy indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$ are listed in Table I. In all structures the final difference map showed no peaks of structural significance. Lists of all observed and calculated structure factors are available as supplementary material.

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(1) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1980**, *19*, 1215.

(2) Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 1381.

(3) Cotton, F. A.; Falvello, L. R.; Murillo, C. A. *Inorg. Chem.* **1983**, *22*, 382.

(4) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 351.

(5) For each compound, the unit cell dimensions of several crystals were determined in order to confirm that only one crystalline isomer exists in the bulk.

(6) All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem, using the SHELX 77 structure determination package.

Table II Positional Parameters and Estimated Standard Deviations[a] for **1**

atom	*x*	*y*	*z*
Mo	0.4748 (1)	0.55517 (9)	0.5959 (1)
I(1)	0.4075 (1)	0.70539 (8)	0.9079 (1)
I(2)	0.0610 (1)	0.4407 (1)	0.2835 (1)
O(1)	0.3869 (8)	0.4603 (7)	0.6344 (9)
O(2)	0.3012 (8)	0.6443 (7)	0.4704 (9)
O(3)	0.6473 (8)	0.4738 (7)	0.7347 (9)
O(4)	0.5564 (8)	0.6560 (7)	0.5645 (9)
N(1)	0.239 (1)	0.362 (1)	0.659 (1)
N(2)	0.120 (1)	0.600 (1)	0.098 (1)
C(1)	0.393 (1)	0.373 (1)	0.544 (2)
C(2)	0.337 (1)	0.298 (1)	0.567 (2)
C(3)	0.438 (2)	0.205 (1)	0.630 (2)
C(4)	0.396 (2)	0.113 (1)	0.629 (2)
C(5)	0.455 (2)	0.058 (2)	0.751 (3)
C(6)	0.422 (3)	−0.034 (2)	0.746 (3)
C(7)	0.335 (3)	−0.060 (2)	0.643 (3)
C(8)	0.275 (3)	−0.07 (2)	0.527 (3)
C(9)	0.307 (2)	0.083 (1)	0.522 (2)
C(10)	0.279 (1)	0.609 (1)	0.330 (1)
C(11)	0.155 (1)	0.673 (1)	0.238 (2)
C(12)	0.176 (1)	0.766 (1)	0.202 (2)
C(13)	0.054 (2)	0.839 (1)	0.115 (2)
C(14)	−0.029 (2)	0.922 (2)	0.191 (3)
C(15)	−0.146 (3)	0.988 (2)	0.095 (5)
C(16)	−0.164 (3)	0.961 (3)	−0.056 (4)
C(17)	−0.078 (3)	0.882 (2)	−0.130 (4)
C(18)	0.035 (2)	0.818 (2)	−0.043 (3)
OW(1)	0.3076 (9)	0.4971 (8)	0.928 (1)
OW(2)	0.164 (1)	0.254 (1)	0.818 (2)
OW(3)	0.304 (2)	0.274 (2)	0.091 (2)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Important Bond Lengths (Å) and Angles (deg) for **I**

Mo-Mo′	2.114 (1)	C(2)-N(1)	1.51 (2)
-I(1)	3.253 (1)	-C(1)	1.52 (2)
-O(1)	2.12 (1)	-C(3)	1.47 (2)
-O(2)	2.112 (7)	C(11)-N(2)	1.51 (1)
-O(3)	2.126 (7)	-C(10)	1.52 (1)
-O(4)	2.10 (1)	-C(12)	1.52 (2)
Mo′-Mo-I(1)	174.53 (7)	O(1)-Mo-O(4)	177.1 (4)
-O(1)	91.3 (3)	O(2)-Mo-O(3)	176.2 (4)
-O(2)	92.8 (3)	-O(4)	89.6 (4)
-O(3)	91.0 (3)	O(3)-Mo-O(4)	89.6 (4)
-O(4)	91.5 (3)	N(1)-C(2)-C(1)	109 (1)
I(1)-Mo-O(1)	85.0 (3)	-C(3)	115 (1)
-O(2)	91.3 (3)	C(1)-C(2)-C(3)	110 (2)
-O(3)	85.0 (3)	N(2)-C(11)-C(10)	108 (2)
-O(4)	92.3 (3)	-C(12)	112 (1)
O(1)-Mo-O(2)	89.2 (4)	C(10)-C(11)-C(12)	107 (1)
-O(3)	91.4 (4)		

Table IV. Positional Parameters and Estimated Standard Deviations[a] for **2**

atom	*x*	*y*	*z*
Mo	−0.01391 (6)	−0.06540 (6)	0.04250 (7)
I(1)	−0.07021 (6)	−0.26758 (6)	0.13534 (8)
I(2)	0.31290 (6)	0.08450 (7)	0.38659 (8)
O(1)	0.1750 (5)	−0.1640 (5)	0.0740 (6)
O(2)	0.0077 (5)	−0.1592 (5)	−0.1798 (6)
O(3)	0.2050 (5)	−0.0265 (5)	−0.0174 (6)
O(4)	0.0334 (5)	−0.0195 (5)	−0.2699 (6)
O(5)	0.9203 (6)	−0.5678 (6)	0.2092 (9)
O(6)	0.6148 (8)	−0.4125 (9)	−0.278 (1)
N(1)	0.4416 (6)	−0.1203 (7)	0.0284 (9)
N(2)	0.0041 (8)	−0.2754 (8)	−0.444 (1)
C(1)	0.2425 (7)	−0.1219 (7)	0.0358 (9)
C(2)	0.3800 (8)	−0.1958 (9)	0.040 (1)
C(3)	0.4167 (9)	−0.261 (1)	0.172 (1)
C(4)	0.5531 (8)	−0.3401 (9)	0.175 (1)
C(5)	0.611 (1)	−0.438 (1)	0.063 (1)
C(6)	0.7344 (9)	−0.5163 (9)	0.070 (1)
C(7)	0.7990 (8)	−0.4928 (8)	0.191 (1)
C(8)	0.7435 (9)	−0.3949 (9)	0.302 (1)
C(9)	0.6215 (9)	−0.3183 (9)	0.293 (1)
C(10)	0.0237 (7)	−0.1127 (8)	−0.2872 (9)
C(11)	0.029 (1)	−0.1739 (8)	−0.453 (1)
C(12)	0.1491 (9)	−0.200 (1)	−0.537 (1)
C(13)	0.2688 (9)	−0.2561 (9)	−0.454 (1)
C(14)	0.315 (1)	−0.369 (1)	−0.421 (1)
C(15)	0.431 (1)	−0.421 (1)	−0.357 (1)
C(16)	0.497 (1)	−0.356 (1)	−0.331 (1)
C(17)	0.452 (1)	−0.242 (1)	−0.358 (1)
C(18)	0.335 (1)	−0.190 (1)	−0.417 (1)
OW(1)	−0.3831 (6)	−0.0434 (6)	0.1904 (8)
OW(2)	0.103 (1)	0.5070 (9)	0.369 (1)
OW(3)	0.3122 (7)	0.2552 (8)	0.1139 (9)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table V. Important Bond Lengths (Å) and Angles (deg) for **2**

Mo-Mo′	2.116 (1)	C(2)-N(1)	1.49 (1)
-I(1)	3.212 (1)	-C(1)	1.53 (1)
-O(1)	2.122 (4)	-C(3)	1.49 (1)
-O(2)	2.126 (5)	C(11)-N(2)	1.49 (1)
-O(3)	2.124 (4)	-C(10)	1.56 (1)
-O(4)	2.127 (5)	-C(12)	1.56 (1)
Mo′-Mo-I(1)	173.46 (4)	O(1)-Mo-O(4)	89.6 (3)
-O(1)	92.3 (1)	O(2)-Mo-O(3)	91.2 (3)
-O(2)	90.7 (1)	-O(4)	176.7 (3)
-O(3)	91.0 (2)	O(3)-Mo-O(4)	89.9 (3)
-O(4)	92.4 (2)	N(1)-C(2)-C(1)	108.7 (1)
I(1)-Mo-O(1)	91.1 (2)	-C(3)	114.3 (8)
-O(2)	83.8 (1)	C(1)-C(2)-C(3)	112.6 (9)
-O(3)	85.6 (2)	N(2)-C(11)-C(10)	107.3 (7)
-O(4)	93.2 (2)	-C(12)	116 (1)
O(1)-Mo-O(2)	89.2 (3)	C(10)-C(11)-C(12)	111.1 (8)
-O(3)	176.7 (2)		

Results and Discussion

The atomic positional parameters of structures **1–3** are listed in Tables II, IV, and VI, while Tables III, V, and VII present the important bond lengths and angles of **1–3**, respectively. The structures and numbering schemes of the dimeric complexes are shown in Figures 1–3. In all three structures there is a crystallographic inversion center between the molybdenum atoms of the dimer and there is only half a $Mo_2[O_2CCH(NH_3^+)R]_4^{4+}$ ion in the asymmetric unit, with the other half related to it by the crystallographic inversion center. The $Mo_2(O_2CC)_4$ cores in structures **1–3** display a nearly D_{4h} symmetry, and the Mo–Mo distances are 2.114 (1), 2.116 (1) and 2.113 (1) Å, respectively, similar to those found in many other $Mo_2(O_2CR)_4$ structures.[7]

In structures **1** and **2**, iodide ions are axially bonded to the Mo–Mo unit with Mo–Mo–I angles of 174.53 (7) and 173.46 (4)°, respectively. The relatively long Mo–I distances [3.253 (4) and 3.212 (1) Å, respectively] are indicative of weak bonding. In structure **3**, a sulfonato oxygen is axially bonded to the Mo–Mo unit with an M–O distance of 2.560 (6) Å and an Mo–Mo–O angle of 178.0 (2)°.

Networks of hydrogen bonding exist in the crystals of the three compounds between the $-NH_3^+$ groups, the water molecules, and the coordinated and uncoordinated anions. In **1** and **2** the I···O and I···N distances are within the normal range of 3.53–3.75 Å, and the O···O and O···N distances in all three structures are in the range of 2.65–2.95 Å.

As can be seen from Figures 1–3, there are intramolecular hydrogen bonds between the $-NH_3^+$ nitrogens and carboxylate oxygens within each of the coordinated amino acids. In all three structures, the deviations of the ammonium nitrogen from the carboxylate planes (defined by O_2CC) are less than 0.5 Å. The four $-NH_3^+$ groups in each compound are arranged

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(7) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982.

Table VI. Positional Parameters and Estimated Standard Deviations[a] for **3**

atom	x	y	z
Mo	1.05611 (7)	−0.04250 (4)	0.94853 (7)
S(1)	1.3247 (2)	−0.1845 (1)	0.8541 (2)
S(2)	0.8012 (3)	−0.1252 (2)	0.3756 (3)
O(1)	0.9445 (5)	0.0165 (3)	0.7500 (5)
O(2)	1.1724 (5)	−0.1076 (3)	1.1405 (6)
O(3)	0.9285 (5)	−0.1238 (3)	0.8960 (5)
O(4)	1.1900 (5)	0.0346 (3)	0.9943 (5)
O(5)	1.3761 (6)	−0.1724 (4)	0.7471 (6)
O(6)	1.4043 (6)	−0.1637 (4)	0.9936 (6)
O(7)	1.1899 (5)	−0.1417 (4)	0.8172 (7)
O(8)	0.739 (1)	−0.1421 (5)	0.2308 (8)
O(9)	0.7105 (9)	−0.0688 (5)	0.428 (1)
O(10)	0.9141 (8)	−0.0932 (6)	0.409 (1)
N(1)	1.3780 (6)	0.1116 (4)	1.0586 (8)
N(2)	0.8236 (7)	0.0874 (4)	0.4989 (7)
C(1)	1.1695 (8)	0.0998 (5)	1.0663 (8)
C(2)	1.2741 (8)	0.1497 (5)	1.1223 (9)
C(3)	1.2294 (8)	0.2422 (5)	1.0969 (9)
C(4)	1.304 (1)	0.2935 (7)	1.187 (1)
C(5)	1.267 (1)	0.3816 (8)	1.163 (1)
C(6)	1.159 (1)	0.4141 (8)	1.053 (1)
C(7)	1.084 (1)	0.3644 (8)	0.962 (1)
C(8)	1.120 (1)	0.2759 (7)	0.984 (1)
C(9)	0.8558 (8)	0.0787 (5)	0.7508 (9)
C(10)	0.7633 (8)	0.1185 (5)	0.6093 (9)
C(11)	0.7335 (9)	0.2138 (6)	0.618 (1)
C(12)	0.827 (1)	0.2555 (8)	0.632 (1)
C(13)	0.793 (2)	0.349 (1)	0.636 (2)
C(14)	0.671 (2)	0.383 (1)	0.630 (2)
C(15)	0.576 (2)	0.347 (1)	0.609 (2)
C(16)	0.607 (1)	0.2534 (9)	0.605 (1)
C(17)	1.3318 (8)	−0.2926 (5)	0.8565 (8)
C(18)	1.3041 (9)	−0.3224 (6)	0.964 (1)
C(19)	0.312 (1)	−0.4093 (7)	0.966 (1)
C(20)	1.3423 (9)	−0.4626 (6)	0.862 (1)
C(21)	1.367 (1)	−0.4306 (6)	0.756 (1)
C(22)	1.3614 (9)	−0.3449 (6)	0.753 (1)
C(23)	1.353 (1)	−0.5576 (7)	0.868 (1)
C(24)	0.8467 (9)	−0.2201 (6)	0.4666 (9)
C(25)	0.941 (1)	−0.2283 (6)	0.601 (1)
C(26)	0.981 (1)	−0.3056 (7)	0.668 (1)
C(27)	0.929 (1)	−0.3712 (7)	0.606 (1)
C(28)	0.832 (1)	−0.3627 (8)	0.475 (1)
C(29)	0.789 (1)	−0.2850 (7)	0.401 (1)
C(30)	0.978 (1)	−0.4579 (9)	0.678 (1)
OW(1)	1.4560 (8)	−0.0405 (5)	1.1966 (9)
OW(2)	0.460 (1)	0.0862 (8)	0.438 (1)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table VII. Important Bond Lengths (Å) and Angles (deg) for **3**

Mo-Mo′	2.113 (1)	C(2)-N(1)	1.52 (1)
Mo-O(1)	2.130 (4)	-C(1)	1.53 (1)
-O(2)	2.131 (4)	-C(3)	1.51 (1)
-O(3)	2.115 (5)	C(10)-N(2)	1.50 (1)
-O(4)	2.121 (5)	-C(9)	1.53 (1)
-O(7)	2.560 (6)	-C(11)	1.53 (1)
Mo′-Mo-O(1)	91.5 (2)	O(2)-Mo-O(7)	90.0 (2)
-O(2)	91.8 (2)	O(3)-Mo-O(4)	176.7 (2)
-O(3)	92.2 (2)	-O(7)	88.5 (2)
-O(4)	91.0 (1)	O(4)-Mo-O(7)	88.2 (2)
-O(7)	178.0 (2)	N(1)-C(2)-C(1)	107.4 (7)
O(1)-Mo-O(2)	176.6 (2)	-C(3)	110.5 (6)
-O(3)	87.7 (2)	C(1)-C(2)-C(3)	116.1 (9)
-O(4)	91.9 (2)	N(2)-C(10)-C(9)	108.1 (8)
-O(7)	86.7 (2)	-C(11)	111.1 (7)
O(2)-Mo-O(3)	91.4 (2)	C(9)-C(10)-C(11)	111.7 (9)
-O(4)	88.8 (2)		

in the following way: one pair, from neighboring carboxylates (D and L), is hydrogen bonded to oxygen atoms coordinated to the same molybdenum, while the other pair is hydrogen bonded to oxygen atoms coordinated to the other molybdenum.

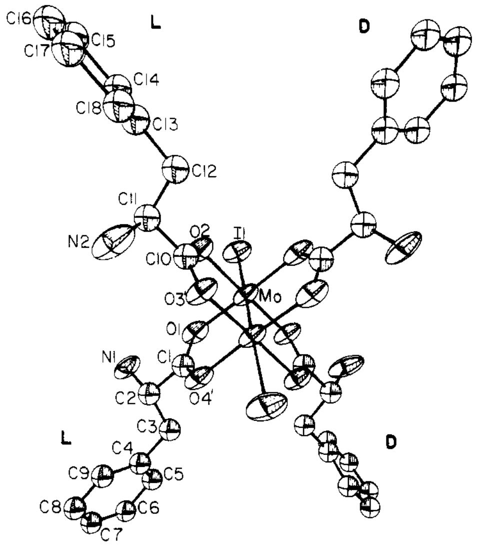

Figure 1. ORTEP drawing of the dinuclear $[Mo_2(D\text{-phe})_2(L\text{-phe})_2I_2]^{2+}$ unit in **1** with thermal ellipsoids enclosing 50% of their electron density. A crystallographic center of inversion is located at the midpoint of the Mo–Mo bond.

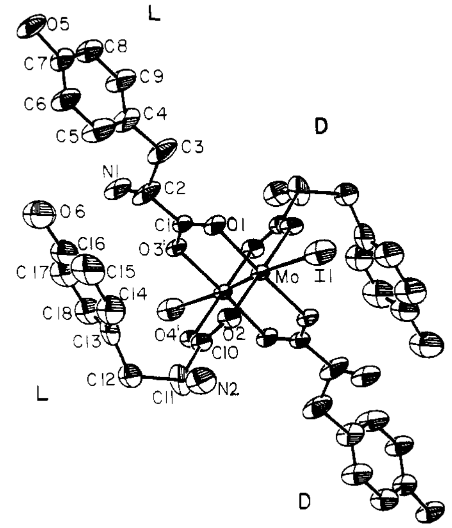

Figure 2. ORTEP drawing of the dinuclear $[Mo_2(D\text{-tyr})_2(L\text{-tyr})_2I_2]^{2+}$ unit in **2** with vibrational ellipsoids drawn at the 50% probability level. The dinuclear molecule resides on a center of inversion.

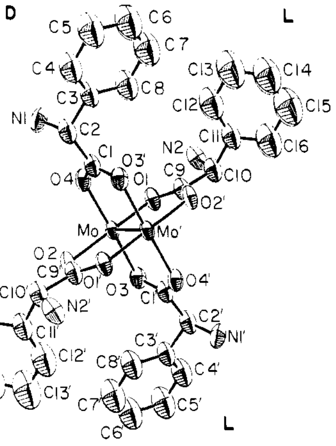

Figure 3. Molecular geometry and atom-labeling scheme for $[Mo_2(D\text{-}C\text{-phgly})_2(L\text{-}C\text{-phgly})_2]^{4+}$. The dinuclear molecule resides on a center of inversion.

This geometry of "right, right, left, left" exists in other dimetal tetrakis α- or β-amino acid complexes such as

$[Mo_2(gly)_4]Cl_4{\cdot}nH_2O$,[8] $[Cr_2(gly)_4]X_4{\cdot}nH_2O$ (X = Cl, Br),[9] and $[Rh_2(\beta\text{-ala})_4](ClO_4)_4{\cdot}2H_2O$.[10] One known exception to this "right, right, left, left" order is the compound $[Mo_2(gly)_4](SO_4)_2{\cdot}4H_2O$,[11] in which the order is "right, left, right, Left". It is notable that this compound is obtained by dissolution of the chloride salt,[8] with "right, right, left, left" arrangement, in aqueous H_2SO_4 under mild conditions.

A priori, the reaction of Mo_2^{4+} with the racemic mixture of the amino acid may yield the following isomers: Mo_2D_4, Mo_2D_3L, Mo_2DDLL, Mo_2DLDL, Mo_2DL_3, and Mo_2L_4. Provided that no steric interactions exist between the chiral centers in the complex $Mo_2D_{4-n}L_n$ (n = 0, 1, 2, 3, 4), it can be shown that the statistical distribution of these isomers in solution should be in the ratio 1:4:4:2:4:1, respectively. Preliminary kinetic results[12] show that the exchange reaction (1) reaches equilibrium rapidly at room temperature (<1 min) whereas the crystallization process is much slower (see Experimental Section). The fact that only one isomer, namely Mo_2DDLL, crystallizes from the solution may be ascribed to a low solubility product of its salts, which shifts the equilibrium in its direction. An alternative reasoning, ascribing this fact to the predominance of the Mo_2DDLL isomer in *solution*, cannot be ruled out, although no support or justification for such an assumption can be offered.

$$Mo_2[O_2CCH(NH_3^+)R]_4 + 4(^-O_2CCH(NH_3^+)R') \rightleftharpoons Mo_2[O_2CCH(NH_3^+)R']_4 + 4(^-O_2CCH(NH_3^+)R) \quad (1)$$

We intend to investigate the isomer distribution in solution by NMR and other techniques.

Registry No. **1**, 90991-54-1; **2**, 90991-55-2; **3**, 90991-58-5; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: Tables of structure factors of structures **1–3**, thermal parameters of compounds **1–3**, and non-essential bond distances and angles within the coordinated amino acids in **1–3** and in the *p*-toluenesulfonate ions in **3** (62 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, State University Leiden, 2300 RA Leiden, The Netherlands, and Interuniversity Reactor Institute, Delft, The Netherlands

Crystal Structure at 300 and 105 K, Magnetic Properties, and Mössbauer Spectra of Bis(triaquatris(4-ethyltriazole-N^1)iron(II)-N^2,$N^{2'}$,$N^{2''}$)iron(II) Hexakis(trifluoromethanesulfonate). A Linear, Trinuclear Iron(II) Compound, Showing a Unique High-Spin–Low-Spin Transition of the Central Iron Atom

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$[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ (Ettrz = 4-ethyl-1,2,4-triazole) is a linear trinuclear coordination compound, in which the two pairs of metal centers are each linked by three 1,2-bicoordinating triazole ligands. The terminal coordination sites are occupied by H_2O molecules. Upon cooling, the central iron(II) undergoes a high-spin to low-spin transition. Mössbauer and magnetic susceptibility data show that this spin crossover gradually takes place between 230 and 190 K. The structural consequences of the spin crossover have been studied by crystal structure determinations at 300 and 105 K. The compound crystallizes in the space group $P\bar{3}1c$, with two trinuclear molecules per unit cell. The lattice constants are $a = b = 14.488$ (5) Å and $c = 19.858$ (5) Å at 300 K and $a = b = 14.265$ (7) Å and $c = 19.632$ (2) Å at 105 K. Fe–O(water) distances at 300 K are 2.156 (4) Å, whereas the Fe–N distances are 2.157 (4) Å (terminal Fe) and 2.174 (4) Å (central Fe). The Fe–L distances of the terminal iron hardly change (0.01–0.02 Å) upon cooling. However, the observed decrease in the Fe–N bond lengths (about 0.14 Å) upon cooling for the central Fe(II) ion reflects a clear strengthening of these bonds in the low-spin state. The low-temperature magnetic susceptibility and Mössbauer data indicate that no magnetic exchange exists between the terminal iron(II) ions.

Introduction

The spin-crossover phenomena in transition-metal chemistry have attracted much attention in recent years. A variety of iron(II) compounds are known to show a transition from the high-spin state (S = 2) to the low-spin state (S = 0) on cooling or upon increasing pressure.[2] A very strong octahedral ligand field is required to induce such a transition, and usually the transition is observed in Fe(II) compounds with chelating nitrogen donor ligands, such as phenanthroline, bipyridyl, and 2-(2-pyridyl)imidazole;[2,3] in addition, the low symmetry as in $Fe(phen)_2X_2$ might aid such a transition.

Recently, we prepared a series of isomorphous linear trinuclear coordination compounds with the composition $[M_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$ (Ettrz = 4-ethyl-1,2,4-triazole) in which M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II).[4-6] The ligand field spectra of the Co and Ni compounds indicated the presence of a strong ligand field in these compounds.[4,6] Because of the asymmetric environment of the outer ions and the expected strong field affecting the central metal ion, the Fe(II) compound was studied in detail in order to investigate the possibility of high-spin–low-spin transitions. The results

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