Structural Studies of Bis(cyclopentadienyl)molybdenum-Amino Acid Complexes

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Abstract. The crystal structures of molybdocene-amino acid compounds of the type $[Cp_2Mo^{IV}(\kappa N,\kappa O\text{-AA})]^+Cl^-\cdot xH_2O$ with AA = D-phenylalaninato (x = 1.5), DL-leucinato (x = 2) and DL-valinato (x = 1) have been determined (Cp = η^5-C_5H_5). The compounds feature an almost planar, five-membered chelate ring of the aminocarboxylate moiety (deprotonated amino acid) with the molybdenum atom. In the phenylalaninato complex π-stacking between the phenyl rings is found. The complexes were proven kinetically stable at pH < 1 for at least 24 h.

Keywords: Molybdocene; Molybdenum; Amino acids; Crystal structure, pi-Stacking

Strukturuntersuchungen an Bis(cyclopentadienyl)molybdän-Aminosäure-Komplexen

Inhaltsübersicht. Die Kristallstrukturen von Molybdocen-Aminosäure-Verbindungen des Typs $[Cp_2Mo^{IV}(\kappa N,\kappa O\text{-AA})]^+Cl^-\cdot xH_2O$ mit AA = D-Phenylalaninato (x = 1.5), DL-Leucinato (x = 2) und DL-Valinato (x = 1) wurden bestimmt (Cp = η^5-C_5H_5). Die Verbindungen zeigen einen fast ebenen, fünf-gliedrigen Chelatring der Aminocarboxylat-Gruppe (deprotonierte Aminosäure) mit dem Molybdänatom. Im Phenylalaninato-Komplex wird eine π-Stapelung zwischen den Phenylringen gefunden. Die Komplexe erwiesen sich bei pH < 1 für wenigstens 24 h als kinetisch stabil.

Introduction

Molybdocene dichloride, Cp_2MoCl_2 (Cp = η^5-C_5H_5, η^5-cyclopentadienyl) belongs to the class of metallocene dihalides Cp_2MX_2 with M = Ti, Mo, Nb, V and X = halide which show high antiproliferative properties against diverse animal and human tumors [1, 2, 3, 4, 5]. Yet, there are pronounced differences between these early metallocenes in their behavior under physiological conditions: (1) The Cp-Ti bond is unstable towards hydrolysis [6], the Cp_2Mo fragment is rather water stable. Hydrolysis of olive-green Cp_2MoCl_2 yields dark-red $[Cp_2Mo(OH)(OH_2)]^+$ or $[Cp_2Mo(OH_2)_2]^{2+}$ cations with a concomittant decrease of the pH from 7 to 2 in the solution due to the formation of HCl. The hydrolysis of the cyclopentadienyl rings is negligible [7, 8]. (2) In titanocene compounds with α-amino acids the latter coordinate solely through an oxygen atom of the carboxylate group in the structurally elucidated complexes which then have the formula $[Cp_2Ti(\kappa O\text{-AA})_2]^{2+}$ (AA = deprotonated α-amino acid = α-aminocarboxylate) [9, 10]. In the binding of Cp_2M (M = Ti, Zr) to tripeptide derivatives a chelate formation has, however, been suggested [11]. The first molybdocene−amino acid compounds, $[Cp_2Mo(AA)]^+$ seem to have been prepared by Gore and Green [12] and an *N,O*-chelate binding of the aminocarboxylate ligand to molybdenum had subsequently been proven by structural characterization through single-crystal X-ray diffraction of the L-prolinato- and L-leucinato-molybdocene compound as the hexafluorophosphate salt [13]. Except for this rather early publication no further Cp_2Mo−amino acid complexes seem to have been reported as revealed by a search of the Cambridge Structure Database [14]. Within the field of organometallic metal complexes with biologically important amino acid derivatives or peptide ligands [11, 15, 16, 17] we therefore describe here the structure of three molybdocene−amino acid compounds of the type $[Cp_2Mo(\kappa N,\kappa O\text{-AA})]^+Cl^-$ with AA = D-phenylalaninato, DL-leucinato and DL-valinato.

Results and Discussion

Preparation of the molybdocene−amino acid derivatives followed a procedure by *Gore* and *Green* [12]. Bis(η^5-cyclopentadienyl)molybdenum(IV) dichloride, $Cp_2Mo^{IV}Cl_2$, is reacted in degassed water under inert gas with equimolar amounts of amino acid and the base triethylamine under reflux to afford the red bis(cyclopentadienyl)(aminocarboxylato)molybdenum(IV) chloride products, $[Cp_2Mo(AA)]^+Cl^-$ (eq. (1)). Purification proceeded through column chromatography on alumina. Single crystals were obtained from a methanol or dichloromethane solution. The compounds are air- and moisture-stable. They show very good solubility in water and methanol, less so in diethyl ether and dichloromethane. As amino acids D-phenylalanine, DL-leucine and DL-valine (with no additionally functionality in the side arm) were succesfully employed to give single crystals of the molybdenum adduct.

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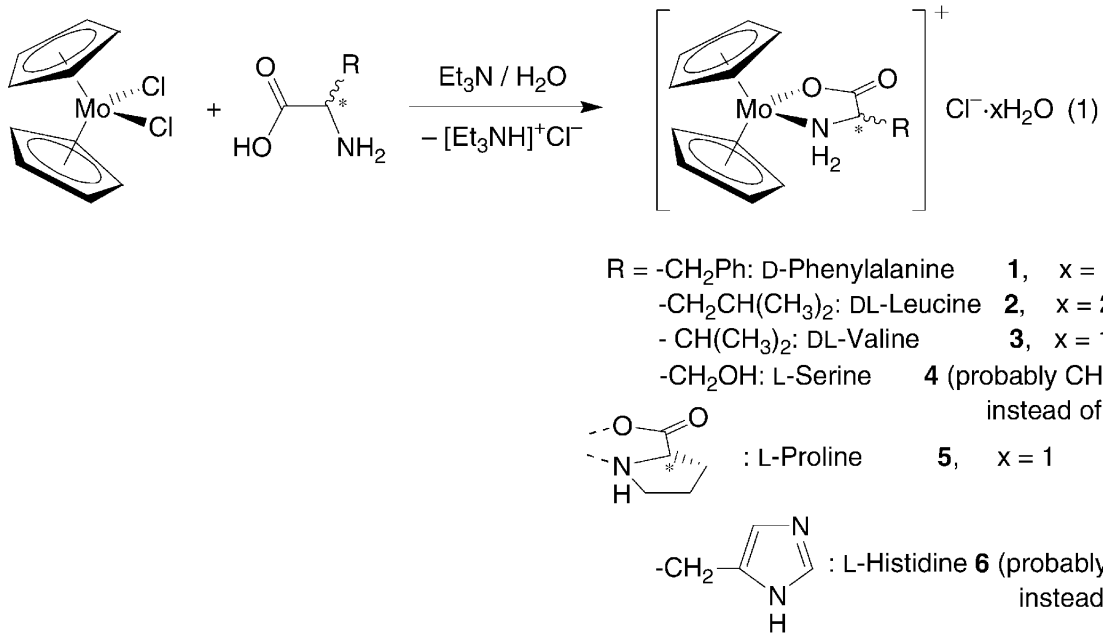

The α-amino acids L-proline, L-histidine and L-serine, the latter two with functional side groups, were also used but failed to give good quality crystals.

Still, the molybdocene–amino acid derivatives were difficult to purify. Even after column chromatography, NMR and ESI-MS analysis showed residues of the side product triethylammonium chloride, $[Et_3NH]^+Cl^-$.

Single-crystal X-ray diffraction proved the suggested [12] chelate formation of the aminocarboxylate (deprotonated amino acid) to the molybdenum atom of the Cp_2Mo^{IV} fragment for compound **1-3** (Fig. 1–3). The five-membered aminocarboxylate chelate ring with molybdenum is planar within (largest deviation) ±0.08 Å in **1**, ±0.12 Å in **2**, and ±0.11 Å in **3**. Selected distances for the molybenum–aminocarboxylate moiety are compared in Table 1. The chloride ion is mostly hydrogen-bonded to the amino group. The compounds crystallize with different amounts of water which complements the hydrogen bonding to the chloride ion (in **1** and **3**). Further hydrogen bonding is found between the water of crystallization and the carboxylate group (in **2** and **3**) and from the amino group to the carboxylate group and crystal water (in **1**). Part of the hydrogen-bonding interactions are depicted in Figures 1-3. The *N,O*-chelate formation of the aminocarboxylate ligand with molybdenum is as seen in the molybdocene compounds $[Cp_2Mo^{IV}$(L-prolinato)$]^+PF_6^-$ and $[Cp_2Mo^{IV}$(L-leucinato)$]^+PF_6^-$ [13] and in the isoelectronic half-sandwich molybdenum compounds $[CpMo^{II}(CO)_2$(DL-serinato)] [18] and $[CpMo^{II}(NO)(I)(\kappa N,\kappa O$-L-$H_2NCH(^tBu)COO)]$ [19]. Additional half-sandwich molybdenum–aminocarboxylate compounds have been prepared but not structurally characterized [15, 20]. In a molybdenum(VI) peroxo–α-amino acid complex the zwitterionic amino acids alanine and proline are bound through the carboxylate group only [21].

The intermolecular packing between the two independent molecules in **1** is controlled by typical π-stacking interactions [22] between the phenyl planes (Fig. 1). The two different phenyl ring planes are almost parallel with a small dihedral angle of 3°. The ring slippage is typical with a slip angle of 22.5° or 24.4° (depending on which phenyl is taken as the reference plane). This corresponds to a vertical displacement between the ring centroids of 1.53 Å (centroid separation 3.847 Å, interplanar distance 3.51 or 3.55 Å, respectively) [22, 23, 24]. The shortest carbon contact is C19-C39 = 3.50(1) Å.

The three molybdocene–amino acid complexes were investigated by potentiometric titration for their thermodynamic stability. Each complex was dissolved in water, the solution set to a pH of 2.3 with HCl and titrated with 0.1 mol/L NaOH. Data analysis revealed that there was no competition reaction between the proton and a metal species for a ligand. An inverse potentiometric titration where the solution of the compound was set to pH = 11.5 with NaOH followed by titration with 0.1 mol/L HCl gave the same result. However, while acid/base reactions are generally fast, metal-ligand exchanges can be very slow. Direct titration methods are only suitable for reasonably labile metal species, in order to be completed in a reasonable timeframe. Thus, we have to conclude that the molybdocene–amino acid complexes **1-3** are kinetically stable (inert) in a pH range from 2.3-11.5. This conclusion was tested and verified further with the molybdocene–valinato complex **3** using time-dependent UV-VIS, ^{13}C NMR and ESI-MS measurements. An aqueous solution of **3** with a pH set to 1.0 by addition of conc. HNO_3 (UV-VIS) or a pH set to 0.08 by addition of conc. HCl (^{13}C NMR, ESI-MS) was monitored for 24 h by the above spectroscopic techniques. No changes were apparent in the UV-VIS, ^{13}C

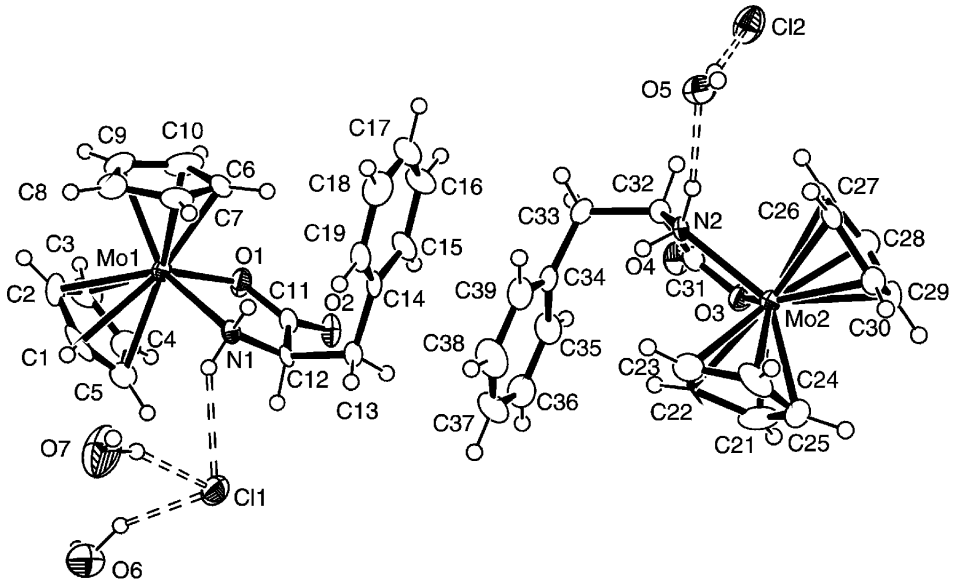

Fig. 1 Molecular structure of the two symmetry-independent molecules in **1** with part of their hydrogen bonding interactions and their π-stacking orientation:
(N1-)H···Cl1 2.46 Å (143°), (O7-)H···Cl1 2.24(8) (159(9)°), (O6-)H···Cl1 2.21(6) (153(6)°), (N2-)H···O5 1.94 (165°), (O5-)H···Cl2 2.21(7) (177(5)°).

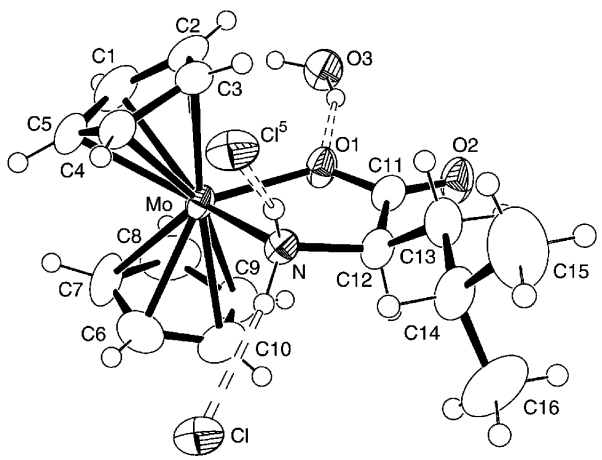

Fig. 2 Molecular structure of **2** with part of its hydrogen bonding interactions:
(N-)H···Cl 2.35 Å (164°), (N-)H···Cl^5 2.39 (161°), (O3-)H···O1 1.84(6) (159(5)°); symmetry transformation ^{5} = −x+2, −y, −z+2.

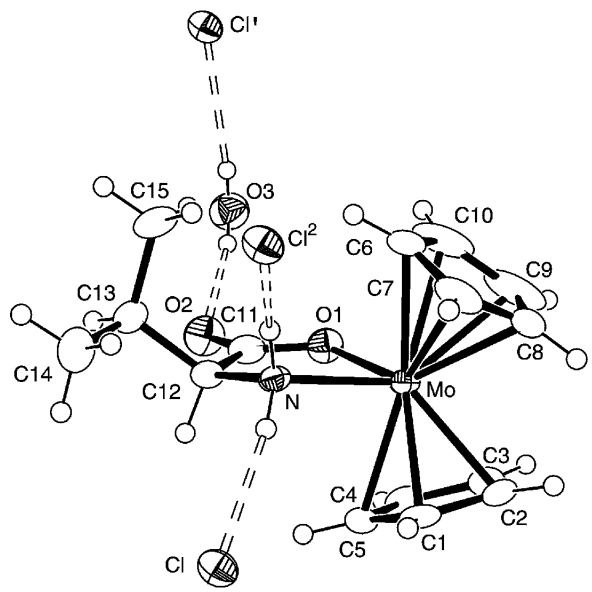

Fig. 3 Molecular structure of **3** with its hydrogen bonding interactions:
(N-)H···Cl 2.38 Å (169°), (N-)H···Cl^2 2.51 (155°), (O3-)H···O2 2.11(4) (171(5)°), (O3-)H···Cl′ 2.52(5) (167(5)°); symmetry transformation ^{2} = −x, −y, −z; ′ = x, y+1, z.

NMR and ESI-mass spectra of such acidified solutions of compound **3**. ESI-MS measurements were extended up to 7 days. After this time some additional molybdenum-containing peaks (according to their isotopic pattern), albeit with an intensity of less than 10 % became apparent, for example m/z = 263 (5 %; $[Cp_2MoCl]^+$).

Experimental

All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or drybox techniques with argon 5.0 (99.999 % purity) as inert gas. Dichloromethane and chloroform were dried over P_4O_{10} or molecular sieve. Methanol and ethanol were dried over molecular sieve. Amino acids (Aldrich) and $MoCl_5$ (Fluka/Merck) were used as received. Dichlorobis(cyclopentadienyl)molybenum(IV), [molybdocene dichloride, $(\eta^5\text{-}C_5H_5)_2MoCl_2$, Cp_2MoCl_2] was prepared via the dihydride, Cp_2MoH_2 [25] as described in the literature [26, 27, 28].

Elemental analyses were obtained on a VarioEL from Elementaranalysensysteme GmbH. IR spectra (2-4 mg compound/300 mg KBr pellet) were measured on a Bruker Optik IFS 25. NMR spectra were recorded on a a Varian Unity-300 spectrometer (300.1 MHz for ^{1}H) with calibration against the solvent signal

Table 1 Selected bond distances/Å and angles/° for the $[Cp_2Mo(AA)]^+$ moiety in **1-3** (AA = deprotonated α-amino acid, aminocarboxylate).

	1[a] AA = L-phenylalaninato	**2** DL-leucinato	**3** DL-valinato
Mo-O1	2.098(2)	2.102(3)	2.098(2)
Mo-N	2.211(6)	2.198(3)	2.216(2)
Mo-C(Cp)	2.31(6)	2.31(5)	2.31(7)
Mo-Ct1[b]	1.983(1)	1.987(2)	1.977(2)
Mo-Ct2[b]	1.977(2)	1.980(3)	1.980(2)
Mo-Cp1 plane[c]	1.978(1)	1.9838(3)	1.9735(2)
ring slippage1[d]	0.134(5)	0.116	0.127
Mo-Cp2 plane[c]	1.973(4)	1.9763(3)	1.9781(2)
ring slippage2[d]	0.116(30)	0.127	0.089
O1-Mo-N	75.8(5)	75.2(1)	75.42(8)
Ct1-Mo-Ct2	133.7(10)	135.9(1)	134.22(7)
Ct1-Mo-O1	107.1(12)	107.5(1)	108.28(7)
Ct2-Mo-O1	108.3(2)	106.7(1)	106.72(9)
Ct1-Mo-N	108.3(10)	109.1(1)	107.37(7)
Ct2-Mo-N	108.7(2)	106.0(1)	109.29(8)
N-C-C-O1[e]	9(2)	9.4(5)	7.7(3)

[a] average values with range in parentheses for the two independent molecules for **1**. – [b] Ct = ring centroid: Ct1 from ring C1-C2-C3-C4-C5; Ct2 from ring C5-C6-C7-C8-C9-C10. – [c] perpendicular projection of Mo atom on Cp (C_5H_5) plane. – [d] ring slippage = distance between perpendicular projection of Mo atom on Cp plane and ring centroid. – [e] Torsion angle.

(D_2O 4.87 ppm). UV-VIS spectra were collected with a Polytec diode-array spectral photometer X-dab equipped with wave-guide optic and an immersion probe head (10 mm light path) in the 300-1000 nm range. ESI-MS measurements were carried out using a Finnigan MAT TSQ7000 spectrometer with methanol or methanol/water being the solvent. Mass spectra were measured in positive ion mode. Molybdenum containing ions had a clearly visible metal isotope pattern [24a], arising from the distribution: ^{92}Mo 14.84 %, ^{94}Mo 9.25 %, ^{95}Mo 15.92 %, ^{96}Mo 16.68 %, ^{97}Mo 9.55 %, ^{98}Mo 24.13 %, ^{100}Mo 9.63 % [29]. Mass peaks listed refer to fragments with the isotopes ^{1}H, ^{12}C, ^{16}O, ^{35}Cl and ^{98}Mo. Potentiometric titrations were carried out with a Metrohm 665 Dosimat (1 mL burette Metrohm 535-138) using a Metrohm combined glass electrode with internal Ag/AgCl reference. Data analysis was done as described before [30].

[Bis(η^5-cyclopentadienyl)(*κN,κO*-D(*R*)-phenylalaninato)molybdenum(IV)]chloride-1.5hydrate, $[(\eta^5\text{-}C_5H_5)_2Mo(\kappa N,\kappa O\text{-D}(R)\text{-}H_2NCH(CH_2Ph)COO)]Cl \cdot 1.5H_2O$ (1). D-Phenylalanine (0.83 g, 5.0 mmol) was suspended under inert gas in 40 mL of degassed water and dissolved completely upon additon of triethylamine (0.7 mL, 5.0 mmol). To this colorless solution was added Cp_2MoCl_2 (1.50 g, 5.0 mmol) and the resulting olive-green slurry was heated to reflux for 2 d until a dark-red solution with a brown precipitate had developed. The reaction mixture was filtered and the dark-red filtrate was evaporated to dryness under vacuum. The residue was dissolved in a small amount of methanol, filtered and brought onto an alumina B column made up with CH_2Cl_2. Elution started with CH_2Cl_2, followed by diethyl ether and finally methanol which eluted a dark-red band containing the product. The solvent was removed under vacuum to leave a dark-red powder which is air- and moisture-stable (yield 1.53 g, 68 %). Crystals suitable for X-ray diffraction could be grown by slow solvent evaporation from the methanol solution. Calc for the hydrate $C_{19}H_{23}ClMoNO_{3.5}$ (452.77): C 50.40, H 5.12, N 3.09. Found C 50.68, H 6.32, N 4.22 %.

IR: 3422s, 3071m, 3056m (CH), 2950w, 2678w, 2496w, 2380w, 2250w, 1647vs ($CO_{2,asym}$), 1595s, 1577m ($NH_{2,asym}$), 1433w, 1357m ($CO_{2,sym}$), 1312w, 1262w, 1172w, 1035w, 886w, 825w, 749w, 701m.
^{1}H NMR (D_2O): δ 2.95-3.25 (m, 2H, CH_2, J_1= 3 Hz; J_2= 5 Hz), 3.45 (t, 1H, N-CH-COO, J= 5 Hz), 5.48 (s, 5H, C_5H_5), 5.80 (s, 5H, C_5H_5), 7.2 (dd, 3H, C_6H_5, J_1= 2 Hz; J_2= 7.7 Hz), 7.4(m, 2H, C_6H_5, J_1= 2.3 Hz; J_2= 7.5 Hz).
ESI-MS: 392 (100 %, $[(C_5H_5)_2Mo(H_2NCH(CH_2Ph)COO)]^+$), 239 (20, $[(Et_3NH)_2Cl]^+$).

[Bis(η^5-cyclopentadienyl)(*κN,κO*-DL-leucinato)molybdenum(IV)]-chloride-dihydrate, $[(\eta^5\text{-}C_5H_5)_2Mo(\kappa N,\kappa O\text{-DL-}H_2NCH\{CH_2CH(CH_3)_2\}COO)]Cl \cdot 2H_2O$ (2). Preparation as for **1** from DL-leucine (0.44 g, 3.36 mmol), triethylamine (0.47 mL, 3.36 mmol) and Cp_2MoCl_2 (1.0 g, 3.36 mmol) as a dark-red solid which is air- and moisture-stable (yield 0.78 g, 60 %). Crystals suitable for X-ray diffraction could be grown by slow solvent evaporation from the methanol solution. Calc for the anhydride $C_{16}H_{22}ClMoNO_2$ (391.73): C 49.06, H 5.66, N 3.57. Found C 51.87, H 6.57, N 3.08 %.

IR: 3421m, 3093m, 2954m, 1647vs ($CO_{2,asym}$), 1600m,sh ($NH_{2,asym}$), 1468w, 1422w, 1366m ($CO_{2,sym}$), 1331m, 1244w, 1211w, 1070w, 992w, 917w, 841m, 559m.
^{1}H NMR (D_2O): δ 0.85 (dd, 6H, CH_3, J = 3.5 Hz), 1.4-1.7 (m, 3H, CH_2 + CH_2-CH-$(CH_3)_2$, J = 6 Hz), 3.15 (t, 1H, N-CH-COO, J = 5 Hz), 5.80 (s, 10H, C_5H_5).
ESI-MS: 358 (100 %, $[(C_5H_5)_2Mo(H_2NCH\{CH_2CH(CH_3)_2\}COO)]^+$).

[Bis(η^5-cyclopentadienyl)(*κN,κO*-DL-valinato)molybdenum(IV)]-chloride-monohydrate, $[(\eta^5\text{-}C_5H_5)_2Mo(\kappa N,\kappa O\text{-DL-}H_2NCH\{CH(CH_3)_2\}COO)]Cl \cdot H_2O$ (3). Preparation as for **1** from DL-valine (0.20 g, 1.69 mmol), triethylamine (0.23 mL, 1.68 mmol) and Cp_2MoCl_2 (0.5 g, 1.68 mmol) as a dark-red solid which is air- and moisture-stable (yield 0.49 g, 74 %). Crystals suitable for X-ray diffraction could be grown by slow solvent evaporation from the methanol solution. Calc for the hydrate $C_{15}H_{22}ClMoNO_3$ (395.73): C 45.53, H 5.60, N 3.54. Found C 45.62, H 5.78, N 3.76 %.

IR: 3426m, 3087m, 2962w, 1644vs, 1599m, 1421w, 1364m, 1338s, 1310m, 1255m, 1222m, 1009m, 903w, 847m, 797w, 554w, 475w.
^{1}H NMR (D_2O): δ 0.80 (d, 3H, CH_3, J = 7 Hz), 0.95 (d, 3H, CH_3, J = 7 Hz), 2.2 (m, 2H, CH-$(CH_3)_2$, J_1 = 7 Hz; J_2 = 3 Hz), 3.05 (d, 1H, N-CH-COO, J = 3.3 Hz), 5.83 (s, 5H, C_5H_5), 5.85 (s, 5H, C_5H_5).
^{13}C NMR (D_2O): δ 14.1 (CH_3), 16.8 (CH_3), 29.8 (*C*H(CH_3)$_2$), 58.2 (N-*C*H-COO), 100.4 (C_5H_5), 101.2 (C_5H_5), 185.9 (*C*OO).
UV-VIS: λ 380, 540 (sh) nm.
ESI-MS: 344 (100 %, $[(C_5H_5)_2Mo(H_2NCH\{CH(CH_3)_2\}COO)]^+$), 239 (5, $[(Et_3NH)_2Cl]^+$), 102 (30, $[Et_3NH]^+$).

[Bis(η^5-cyclopentadienyl)(L-serinato)molybdenum(IV)]methoxide, $[(\eta^5\text{-}C_5H_5)_2Mo(\text{L-}H_2NCH\{CH_2OH\}COO)]OCH_3$ (4). Preparation as for **1** from L-serine (0.26 g, 2.50 mmol), triethylamine (0.40 mL, 2.50 mmol) and Cp_2MoCl_2 (0.75 g, 2.50 mmol) as a dark-red solid (yield 0.71 g, 78 %). Crystals could be grown by slow solvent evaporation from a methanol solution but were not found suitable for X-ray diffraction. Calc for $C_{14}H_{19}MoNO_4$ (361.24): C 46.55, H 5.30, N 3.87. Found C 45.62, H 5.78, N 3.76 %.

IR: 3421m, 3091w, 2369w, 2342w, 1645vs, 1425w, 1326w, 1263w, 1237w, 1191w, 1072w, 1019w, 841w.
^{1}H NMR (D_2O): δ 3.2 (s, 3H, DOCH_3), 3.35 (t, 1H, N-CH-COO, J = 7.6 Hz), 3.85 (d, 2H, -CH_2OH, J = 7.5 Hz), 5.80 (s, 10H, C_5H_5).
ESI-MS: 332 (93 %, $[(C_5H_5)_2Mo(H_2NCH\{CH_2OH\}COO)]^+$), 239 (14, $[(Et_3NH)_2Cl]^+$), 102 (100, $[Et_3NH]^+$).

[Bis(η^5-cyclopentadienyl)(L-prolinato)molybdenum(IV)]chloride-hydrate, $[(\eta^5\text{-}C_5H_5)_2Mo(\text{L-}HNCH\{CH_2CH_2CH_2\}COO)]Cl \cdot H_2O$ (5). Preparation as for **1** from L-proline (0.23 g, 2.00 mmol), triethylamine (0.28 mL, 2.00 mmol) and Cp_2MoCl_2 (0.30 g, 1.00 mmol) as a dark-red-violet solid which is air- and moisture-stable (yield 0.21 g, 53 %). No crystals could be grown from a methanol solution. Calc for the hydrate $C_{15}H_{20}ClMoNO_3$ (393.70): C 45.76, H 5.12, N 3.56. Found C 45.19, H 5.17, N 3.43 %.

Table 2 Crystal data for $[Cp_2Mo(AA)]^+Cl^-\cdot xH_2O$ (**1-3**).

	1[a] AA = L-phenylalaninato x = 1.5	**2** DL-leucinato x = 2	**3** DL-valinato x = 1
Empirical formula	$C_{19}H_{23}ClMoNO_{3.5}$	$C_{16}H_{26}ClMoNO_4$	$C_{15}H_{22}ClMoNO_3$
Formula weight	452.77	427.77	395.73
Crystal size(mm)	0.32 x 0.14 x 0.12	0.30 x 0.30 x 0.20	0.24 x 0.20 x 0.12
Crystal shape	rectangular prism	square-prism	plate
θ range/°	1.23−28.24	1.57−25.60	1.97−26.10
h; k; l range	−29, 33; −8, 7; −21, 10	−22, 22; −22, 21; −13, 13	−9, 9; −12, 12; −13, 13
Crystal system	monoclinic	tetragonal	triclinic
Space group	*C*2	*P*4/*n*	$P\bar{1}$
a/Å	34.965(4)	18.3294(2)	7.6736(6)
b/Å	6.4547(7)	18.3294(2)	10.4488(8)
c/Å	16.560(3)	11.3000(8)	10.7914(8)
α/°			103.058(1)
β/°	91.842(9)		94.861(1)
γ/°			108.522(1)
V/Å	33735.5(8)	3796.4(4)	787.7(1)
Z	8	8	2
D/g cm^{-3}	1.610	1.497	1.669
F(000)	1848	1760	404
μ/mm^{-1}	0.866	0.849	1.011
Max/min transmission	0.9032/0.7690	0.8486/0.7848	0.8883/0.7934
Measured reflections	5656	28744	6346
Unique reflections (R_{int})	5042 (0.0215)	3589 (0.1282)	3057 (0.0392)
Observed reflections [$I>2\sigma(I)$]	4074	2382	2860
Parameters refined	478	230	196
Max/min $\Delta\rho$/e Å^{-3} [b]	1.157/−1.313 [f]	1.059/−0.770 [g]	1.215/−1.211 [f]
*R*1/*wR*2 [$I>2\sigma(I)$] [c]	0.0366/0.0837	0.0465/0.1275	0.0339/0.0876
*R*1/*wR*2 (all data) [c]	0.0479/0.0891	0.0728/0.1388	0.0366/0.0891
Goodness-of-fit on F^2 [d]	0.984	0.936	1.059
Weighting scheme w; *a*/*b* [e]	0.0478/0.0000	0.0848/0.0000	0.0684/0.1040
Absolute structure parameter (Flack value [36])	0.07(5)	–	–

[a] Two symmetry independent molecules in the unit cell. – [b] Largest difference peak and hole. – [c] $R1 = [\Sigma(\|F_o\|-\|F_c\|)/\Sigma|F_o|^\circ]$; $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. – [d] Goodness-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$. – [e] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$. – [f] In the vicinity (<1.2 Å) of the molybdenum atom. – [g] In the vicinity of the disordered water molecules.

IR: 3419m, 3079m, 2977m, 2942m, 2739w, 2676m, 2603s, 2530w, 2496s, 2356w, 1644s, 1475m, 1444m, 1397m, 1383m, 1363m, 1298m, 1266mw, 1172m, 1072w, 1036m, 922w, 850m, 807w, 629w.
^{1}H NMR (D_2O): [aminocarboxylate: HN-CH$^\alpha$-{CH$^\beta_2$-CH$^\gamma_2$-CH$^\delta_2$}-COO] δ 1.5-2.0 (dd, 2H, H$^\gamma$, $J_{\gamma,\beta}$ = 8 Hz, $J_{\gamma,\delta}$ = 11 Hz), 2.2 (t, 2H, H$^\delta$, $J_{\delta,\gamma}$ = 11 Hz), 2.5 (dd, 2H, H$^\beta$, $J_{\beta,\alpha}$ = 11 Hz, $J_{\beta,\gamma}$ = 8 Hz), 3.6 (t, 1H, H$^\alpha$, $J_{\alpha,\beta}$ = 11 Hz), 5.95 (s, 10H, C_5H_5).
ESI-MS: 342 (100 %, $[(C_5H_5)_2Mo(HNCH\{CH_2CH_2CH_2\}COO)]^+$).

[Bis(η^5-cyclopentadienyl)(L-histidinato)molybdenum(IV)]chloride-CH_2Cl_2, $[(\eta^5\text{-}C_5H_5)_2Mo(L\text{-}H_2NCH\{CH_2\text{-}C_3H_3N_2\}COO)]Cl \cdot CH_2Cl_2$ (6). Preparation as for **1** from L-histidine (0.26 g, 2.67 mmol), triethylamine (0.20 mL, 1.67 mmol) and Cp_2MoCl_2 (0.50 g, 1.67 mmol) as a dark-red solid (yield 0.62 g, 74 %). Crystals could be grown by slow solvent evaporation from a methanol solution but were not found suitable for X-ray diffraction. Calc for the CH_2Cl_2 adduct $C_{17}H_{21}Cl_3MoN_3O_2$ (501.49): C 40.70, H 4.22, N 8.37. Found C 40.54, H 4.28, N 8.40 %.

IR: 3419s, 3094s, 2976m, 2603m, 2495m, 1652s, 1475w, 1429w, 1383w, 1309w, 1267w, 1171w, 1079w, 1035w, 849w, 622w, 559m, 493w.
^{1}H NMR (D_2O): δ 3.2 (d, 2H, -CH_2-, J = 7.5 Hz), 3.5 (t, 1H, N-CH-COO, J = 7.6 Hz), 5.75 (s, 5H, C_5H_5), 5.95 (s, 5H, C_5H_5), 7.1 (s, 1H, -C=CH-N-), 7.85 (s, 1H, -N-CH=N-).

Structure determinations

Data Collection: Bruker AXS with CCD area-detector, temperature 180(2) K, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, double-pass method ϕ-ω-scan, Data collection and cell refinement with SMART [31], data reduction with SAINT [31], experimental absorption correction with SADABS [32]. *Structure Analysis and Refinement*: The structure was solved by direct methods (SHELXS-97) [33]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [33].

All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on the cyclopentadienyl and phenyl rings, the amino and methylene group, the methine and methyl carbon were placed at calculated positions, using appropriate riding models (AFIX 43, AFIX 23, AFIX 13, and AFIX 33, respectively) and an isotropic temperature factor of Beq = 1.2 Beq(C/N). In **1** there are two independent molecules per unit cell. Also in **1** the hydrogen atoms of the water molecules were found and refined with Beq = 1.2 Beq(O) and with the O-H bond distances restrained at 0.9(1). In **2** the hydrogen atoms on O3 were found and refined with Beq = 0.08. The second water molecule in **2** is disordered over three positions. The hydrogen atoms on the disordered oxygen atoms O4, O5, and O6 were found but kept at fixed positions for further refinement with Beq = 0.08. For the water molecule of **3**, the hydrogen atoms were found and refined with Beq = 1.2 Beq(O) and the hydrogen bond distances restrained at 0.9(1).

Graphics were obtained with ORTEP 3 for Windows [34]. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown as spheres of arbitrary radii. Supramolecular interactions (π-contacts, hydrogen bonds) were computed with SHELXL or PLATON for Windows [35]. Crystal data and details on the structure refinement are given in Table 2. The structural

data has been deposited with the Cambridge Crystallographic Data Center (No. CCDC-219337 for **1**, CCDC-219338 for **2**, CCDC-219339 for **3**).

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