Molybdenum carbonyl complexes with pyridylimino acidato ligands†

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Reactions of $[Mo(CO)_4(pip)_2]$ with pyridine-2-carbaldehyde and the appropriate amino ester or amino acid produce complexes with chelated pyridylimino ligands bearing, respectively, an ester (**1**) or carboxylate (**2a,b**, **4**, **5a,b**) pendant arm, the structures of which have been determined by X-ray crystallography. In the case of α-amino acids, the resulting imino carboxylate complexes are unstable towards decarboxylation, this being complete for (*R*)-2-phenylglycine. The products of decarboxylation **3a–c** were isolated and characterized, including X-ray structure determinations for **3b** and **3c**. In contrast, the derivatives of β-alanine (**4**) and 3- and 4-aminobenzoic acids (**5a,b**) are stable towards decarboxylation. The structure determinations show that the pyridyliminocarboxylate complexes crystallize as salts with piperidinium cations, forming hydrogen-bonded ion-pair dimers featuring twelve- or eight-membered rings. Protonation of carboxylate complexes with 2 M HCl in CH_2Cl_2/water yields the corresponding neutral complexes **6a,b** containing a free carboxylic acid functionality.

Introduction

The use of metallic complexes in the labeling of biological molecules is an expanding field[1] which benefits from the development of increasingly accurate techniques for the observation of radioactive,[2] spectroscopic, and luminescence properties.[3] Additionally, metallic complexes are being used as models to gain understanding of key steps of the metabolism such as dehydrations, dehydrogenations or decarboxylations,[4] or as mimics for biological catalysts.[5]

On the other hand, the continuing interest on amino acids as ligands for metal complexes, or as building blocks in organometallic chemistry is stimulated by the expectations of attaching the resulting complexes to biological molecules.[6] We have described recently the use of amino acidate anions as bridging ligands in heterobinuclear complexes containing manganese and molybdenum,[7] and explored the metalation of benzodiazepines in ruthenium complexes.[8] In the course of current studies focussed on pyridyl imino ligands we became interested in using amino acids as convenient blocks to build chelate N–N ligands containing a side arm with a carboxylate functionality. This could be used to occupy a third coordination position in the metal, as a hemilabile tripodal ligand or, alternatively, it could serve as an anchoring point to a biomolecule.

In recent years, Herrick *et al.* have made available a convenient method for the preparation of iminoester complexes of molybdenum[9,10] and rhenium.[11] We thought it would be interesting to test the method for the preparation of complexes containing a carboxylate or free carboxylic acid terminus which would be more capable of establishing supramolecular interactions than their ester analogues. In this paper we wish to report the use of this methodology to prepare a family of molybdenum complexes containing a pendant arm with a free acid or carboxylate functionality, which exhibit interesting solid state structures.

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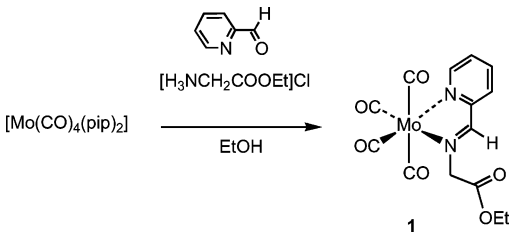
† Dedicated to Dr José A. Abad on occasion of his retirement.

Results and discussion

Pyridylimino glycine ester complex $[Mo(CO)_4(py\text{-}2\text{-}C(H)=NCH_2COOEt)]$ (1)

A mixture of $[Mo(CO)_4(pip)_2]$ (pip = piperidine),[12] pyridine-2-carbaldehyde, and ethylglycine hydrochloride was heated in ethanol (50 °C), to afford $[Mo(CO)_4(py\text{-}2\text{-}C(H)=NCH_2COOEt)]$ (**1**) (Scheme 1), which was isolated as a crystalline solid, and characterized by analytical and spectroscopic methods.



Scheme 1

IR spectra of **1** in CH_2Cl_2 solution display four metal carbonyl bands in the region 2020–1820 cm^{-1} in a pattern consistent with a *cis*-tetracarbonyl geometry. An additional weaker band at 1734 cm^{-1} can be attributed to the ester carbonyl stretches. The pyridine and imine resonances in the ^1H NMR spectra appear as expected. The imine proton resonance at δ 8.49 ppm is most informative since its position is very sensitive to the chemical environment. The presence of the unreacted ester attached to the diimine ligand was confirmed by the signals associated with the ethyl group. No decarboxylation product was observed in the ^1H NMR spectra, in contrast with the carboxylate complexes described below.

The molecular structure of compound **1** was determined by X-ray diffraction on a crystal grown by slow diffusion of a layer of hexane into a solution of **1** in CH_2Cl_2 at −20 °C. Crystallographic and refinement details are summarized in the Experimental section, and a perspective view is presented in Fig. 1.

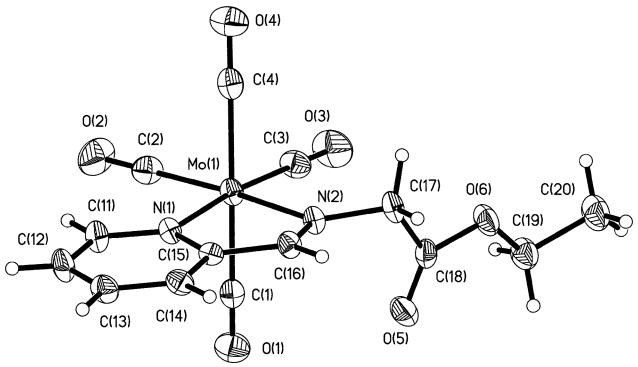


Fig. 1 Perspective view of compound **1** showing the atom numbering. Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 2.022(4), Mo(1)–C(2) 1.934(4), Mo(1)–C(3) 1.939(4), Mo(1)–C(4) 2.023(5), Mo(1)–N(1) 2.238(3), Mo(1)–N(2) 2.231(3), C(18)–O(5) 1.179(4), C(18)–O(6) 1.329(4); C(1)–Mo(1)–C(4) 169.81(13), C(2)–Mo(1)–N(2) 169.79(13), C(3)–Mo(1)–N(1) 173.04(13), N(2)–Mo(1)–N(1) 71.93(10), O(5)–C(18)–O(6) 124.7(4).

The geometry around Mo is slightly distorted octahedral, the main deviation being the small bite angle of the didentate diimine: 71.9(1)°. The pyridine and imine portions of the ligand are essentially coplanar, with the metal atom also lying in the plane. These (otherwise expectable) features are found, without any significant difference, in the structures of the other complexes described below, and will not be further commented.

Complexes derived from α-amino acids and their decarboxylation products

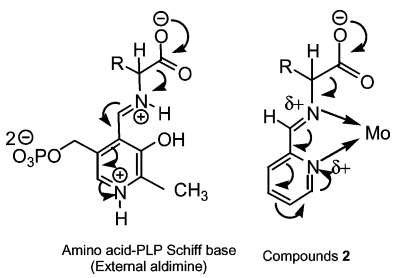
$[Mo(CO)_4(pip)_2]$ was heated (50 °C) with a mixture of pyridine-2-carbaldehyde and a α-amino acid, in ethanol, and the reactions were monitored by IR spectroscopy in solution. After completion, the solvents were evaporated *in vacuo*, and the residue was washed with hexane and then extracted with Et_2O to separate decarboxylation products (see below). The resulting solid residue was recrystallized from dichloromethane/hexane to afford the piperidinium salts **2a** and **2b** (see Scheme 2) as microcrystalline solids. The corresponding decarboxylation products **3a–c** were obtained from the ether extracts. The two series of products can be easily distinguished by their IR and ^{1}H NMR spectra (see Experimental section). It is noteworthy that the extent of decarboxylation depends strongly on the nature of the amino acid as shown in Scheme 2 (percentages were obtained from the ^{1}H NMR spectra of the crude reaction mixtures). In the case of phenylglycine, only the decarboxylation product **3c** was isolated, and no significant amount of the expected carboxylate compound **2c** was observed during the reaction. For alanine and valine, the decarboxylation seems to be slower, and it was possible to isolate the carboxylate complexes **2a** and **2b** with moderate to good yields (see Experimental section).

Suitable crystals could be grown for **2a**, **3b** and **3c**, and the results of the molecular structure determinations are presented in Fig. 2 (compound **2a**), Fig. 3 (**3b**) and Fig. 4 (**3c**). In the three structures, the distorted coordination environment around Mo is similar to that described above for complex **1**.

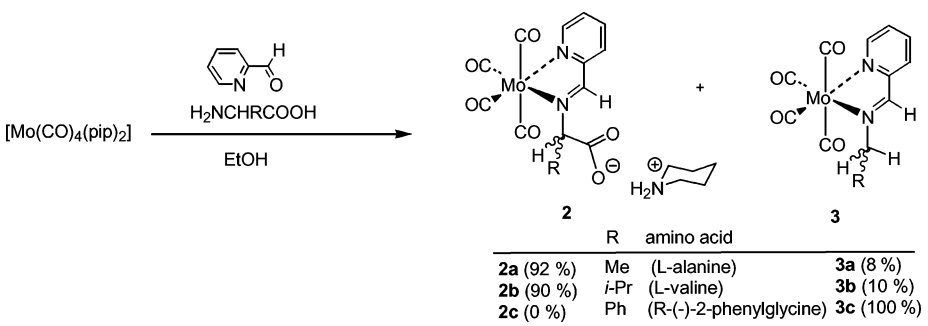
The structure of **2a** shows an interesting arrangement of anion/cation pair dimers, which will be described in detail together with those found in other iminocarboxylate complexes prepared in this work (see below). On the other hand, the high value of the Flack parameter for the structure [0.42(7)] suggests that a nearly total racemization of the chiral α-carbon occurs in the formation of **2a**.

The structures of **3b** and **3c** confirmed the decarboxylation occurred to the parent acidato complexes **2b** and **2c**.

α-Amino acid decarboxylation is a very important step in the synthesis of neurotransmitter amino compounds. The decarboxylation process is thought to take advantage of π-electron delocalization. Coenzyme PLP (pyridoxal-5′-phosphate) reacts with a α-amino acid to form an imine bond between the amino group of the amino acid and the aldehyde group of the PLP. Decarboxylation is produced because PLP functionalities serve as an "electron sink" that stabilizes the developing carbanion in the transition structure attending the loss of CO_2.[13] It has been suggested that the developing negative charge on the α-carbon of the amino acid is delocalized *via* the π-system of the coenzyme bound to the substrate. Scheme 3 offers a comparison of the electron flow in the PLP-assisted enzymatic decarboxylation of amino acids, with that tentatively proposed for complexes **2**, in which the coordination of the pyridinic and iminic N-atoms to the $Mo(CO)_4$ fragment



Scheme 3



Scheme 2

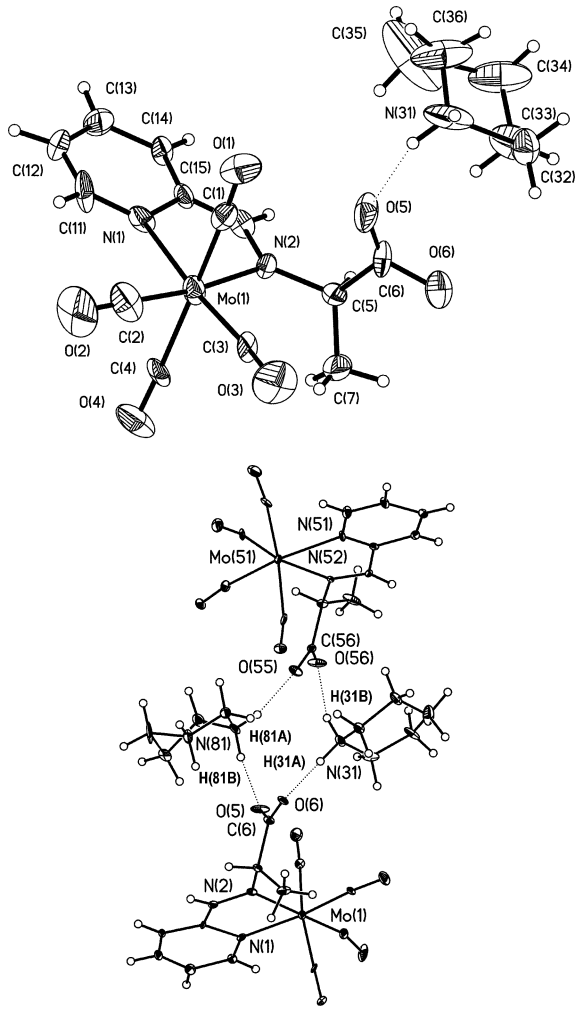


Fig. 2 Perspective view of one of the two independent molecules in the asymmetric unit of compound **2a** showing the atom numbering (above) and ion pair dimerization by hydrogen bonding (below). Selected bond lengths (Å) and angles (°): Molecule 1: Mo(1)–C(1) 1.949(16), Mo(1)–C(2) 1.93(3), Mo(1)–C(3) 1.908(16), Mo(1)–C(4) 1.964(15), Mo(1)–N(1) 2.174(16), Mo(1)–N(2) 2.202(14), C(6)–O(5) 1.10(2), C(6)–O(6) 1.276(19); C(1)–Mo(1)–C(4) 170.3(7), C(3)–Mo(1)–N(1) 173.7(6), C(2)–Mo(1)–N(2) 174.1(9), N(2)–Mo(1)–N(1) 74.0(5), O(5)–C(6)–O(6) 131.5(18). Molecule 2: Mo(51)–C(51) 2.06(2), Mo(51)–C(52) 1.934(13), Mo(51)–C(53) 2.04(2), Mo(51)–C(54) 2.20(2), Mo(51)–N(51) 2.281(13), Mo(51)–N(52) 2.273(13), C(56)–O(55) 1.211(18), C(56)–O(56) 1.291(19); C(51)–Mo(51)–C(54) 174.1(8), C(53)–Mo(51)–N(51) 171.5(8), C(52)–Mo(51)–N(52) 169.5(6), N(52)–Mo(51)–N(51) 71.7(5), O(55)–C(56)–O(56) 119.5(15). Hydrogen bonds: H(31A)···O(6) 1.738(9), N(31)–H(31A)···O(6) 176.83(3), H(31B)···O(56) 1.795(11), N(31)–H(31B)···O(56) 156.26(3), H(81A)···O(55) 1.835(10), N(81)–H(81A)···O(55) 174.43(3), H(81B)···O(5) 1.798(12), N(81)–H(81B)···O(5) 171.62(3).

helps to delocalize the charge towards the metal and, through back-donation, to the good π-accepting carbonyl ligands.

The presence of the electron-withdrawing phenyl group in the α-carbon of the phenylglycine derivative would explain its greater tendency to decarboxylation. The electron withdrawing properties of the coordination to $Mo(CO)_4$ fragment help also to explain the racemization observed for the structure of **2a**.

Within this context, it was expected that the use of amino acids in which the two functionalities were separated by an additional

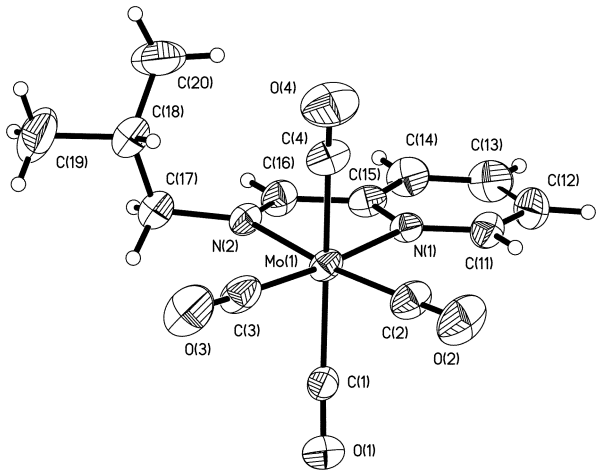


Fig. 3 Perspective view of compound **3b** showing the atom numbering. Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 2.013(5), Mo(1)–C(2) 1.962(5), Mo(1)–C(3) 1.956(5), Mo(1)–C(4) 2.029(5), Mo(1)–N(1) 2.247(3), Mo(1)–N(2) 2.224(3); C(1)–Mo(1)–C(4) 166.35(18), C(2)–Mo(1)–N(2) 171.25(17), C(3)–Mo(1)–N(1) 170.38(16), N(2)–Mo(1)–N(1) 72.65(11).

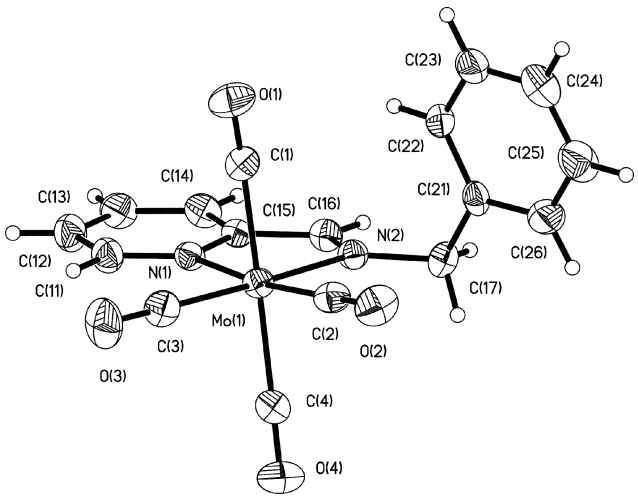
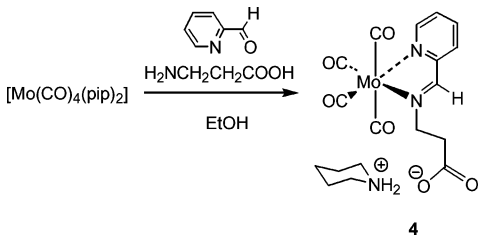


Fig. 4 Perspective view of compound **3c** showing the atom numbering. Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 2.041(4), Mo(1)–C(2) 1.950(4), Mo(1)–C(3) 1.957(4), Mo(1)–C(4) 2.026(4), Mo(1)–N(1) 2.249(2), Mo(1)–N(2) 2.236(2); C(4)–Mo(1)–C(1) 168.72(12), C(3)–Mo(1)–N(2) 169.87(12), C(2)–Mo(1)–N(1) 171.43(11), N(2)–Mo(1)–N(1) 72.50(9).

saturated carbon, or a phenyl group, would help to prevent decarboxylation. To check this point, we used β-alanine and 3-, and 4-amino benzoic acids.

β-Alanine derivative [Hpip][$Mo(CO)_4${py-2-C(H)=NC_2H_4COO}] (4)

[$MoCO)_4(pip)_2$] (pip = piperidine) was heated with a mixture of pyridine-2-carbaldehyde and β−alanine in ethanol, to give [Hpip][$Mo(CO)_4${py-2-C(H)=NC_2H_4COO}] (**4**) (Scheme 4) in good isolated yield. No significant amount of decarboxylation product could be detected from the IR or ^{1}H NMR spectra of the crude reaction mixtures.



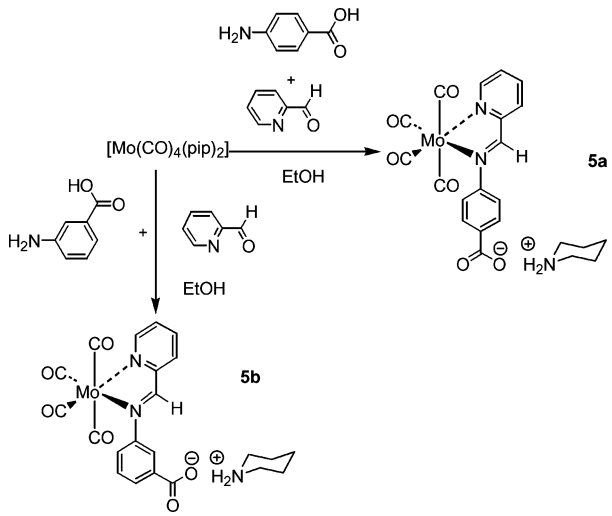
Scheme 4

An X-ray determination (Fig. 5) showed the usual distorted octahedral arrangement of ligands around Mo, as described above for **1**. More interestingly, it was also observed, as for **2a**, dimerization of anion/cation pairs through hydrogen bond formation.

Complexes derived from amino benzoic acids 5a–b

$[Mo(CO)_4(pip)_2]$ was stirred in ethanol at room temperature with pyridine-2-carbaldehyde and the appropriate amino benzoic acid, to afford, after workup, the piperidinium salts **5a** and **5b** (see Scheme 5) as crystalline solids.

The X-ray determinations for **5a** and **5b** (Fig. 6 and 7) showed again the ion-pair dimerization which is present in all the series of piperidinium salts. In the structures of **2a**, **4**, and **5a** the piperidinium cation uses the two hydrogens at the nitrogen atom to



Scheme 5

bind oxygen atoms of two different carboxylate groups. These, in turn, use both oxygen atoms, thus forming a puckered twelve-membered ring. The distances (N–)H···O are in the range 1.7–2.0 Å, and N···O in the range 2.7–2.8 Å. The angles N–H···O lie in the range 165–170°. From these parameters, the hydrogen bonds can be considered as "moderate".[14]

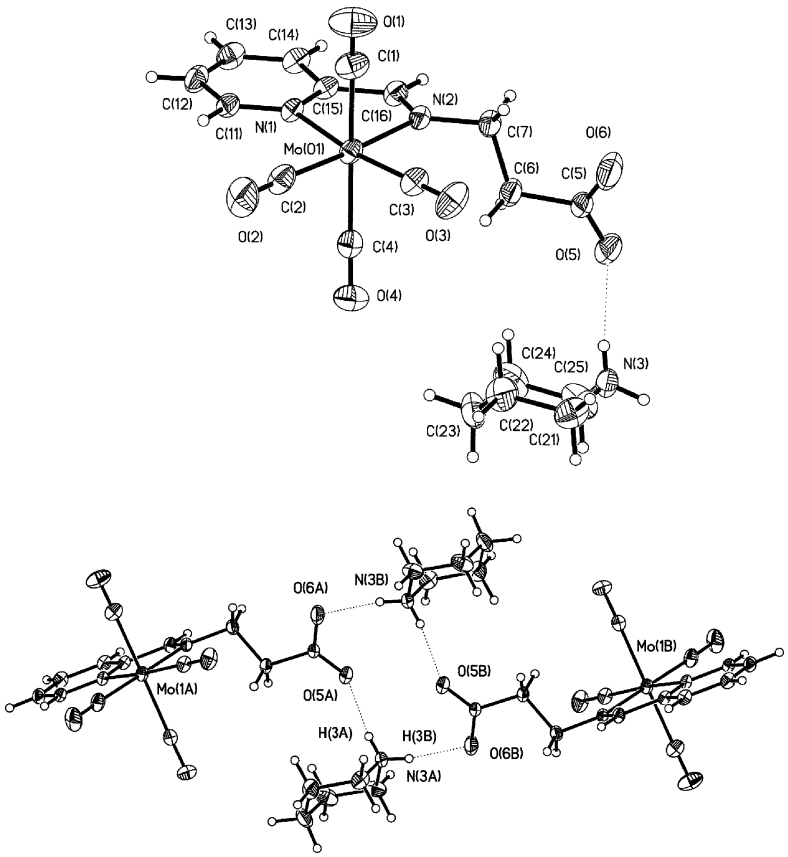


Fig. 5 Perspective view of compound **4** showing the atom numbering (above) and ion pair dimerization by hydrogen bonding (below). Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 2.056(5), Mo(1)–C(2) 1.975(5), Mo(1)–C(3) 1.955(5), Mo(1)–C(4) 2.037(5), Mo(1)–N(1) 2.271(3), Mo(1)–N(2) 2.235(3), C(5)–O(5) 1.215(5), C(5)–O(6) 1.253(5); C(1)–Mo(1)–C(4) 169.25(15), C(3)–Mo(1)–N(1) 170.16(15), C(2)–Mo(1)–N(2) 172.75(15), N(2)–Mo(1)–N(1) 72.35(11), O(5)–C(5)–O(6) 123.1(4). Hydrogen bonds: H(3A)···O(5) 1.896(11), N(3)–H(3A)···O(5) 169.96(3), H(3B)···O(6) 1.808(10), N(3)–H(3B)···O(6) 179.38(3).

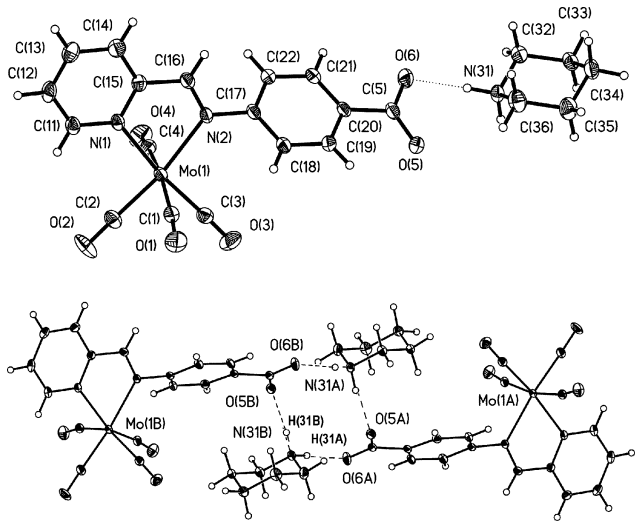


Fig. 6 Perspective view of compound **5a** showing the atom numbering (above) and ion pair dimerization by hydrogen bonding (below). Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 2.054(3), Mo(1)–C(2) 1.960(3), Mo(1)–C(3) 1.968(3), Mo(1)–C(4) 2.025(3), Mo(1)–N(1) 2.256(2), Mo(1)–N(2) 2.251(2), C(5)–O(5) 1.253(4), C(5)–O(6) 1.252(4); C(1)–Mo(1)–C(4) 168.70(12), C(2)–Mo(1)–N(2) 170.89(12), C(3)–Mo(1)–N(1) 172.70(10), N(2)–Mo(1)–N(1) 71.95(8), C(5)–O(6)–O(5) 125.0(3). Hydrogen bonds: H(31A)···O(6) 1.865(12), N(31)–H(31A)···O(6) 172.97(3), H(31B)···O(5) 1.848(10), N(31)–H(31B)···O(5) 171.92(4).

The structure of **5b** is an exception in the series: the dimers are built by using only one of the oxygens of the carboxylate groups, thus forming smaller rings of only eight members. Apart from this, there is a disordered molecule of water (occupancy 0.3), hydrogen bonded to the carboxylate oxygen, and significant C–H(piperidine)···O(carboxyl) interactions (CH···O 2.41 Å, angle C–H···O 160.8°),[15] which could account for the adoption of a different geometry for the dimer in this case.

Protonation of imino acidate complexes

As a test for the stability of the iminocarboxylate complexes against water, and in order to obtain new complexes containing a free carboxylic acid functionality, we carried out a two-phase protonation of **5a** and **2b**. Thus, a stirred solution of compound **5a** or compound **2b** in CH_2Cl_2 was treated with 2 M HCl to afford the compounds **6a,b** (see Scheme 6), which could be isolated in good yields.

An X-ray determination was carried out on a crystal of **6a** (Fig. 8). A remarkable feature of the structure of **6a** is that the dimer ring lies at the twofold axis, rather than at the inversion center, which is considered the "normal" arrangement for carboxylic acids.[16] Such an anomalous case had been found earlier in the structure of 3,5-dinitrocinnamic acid,[17] and it had been attributed to the existence of additional intermolecular C–H···O bonds, which apparently are absent in **6a**.

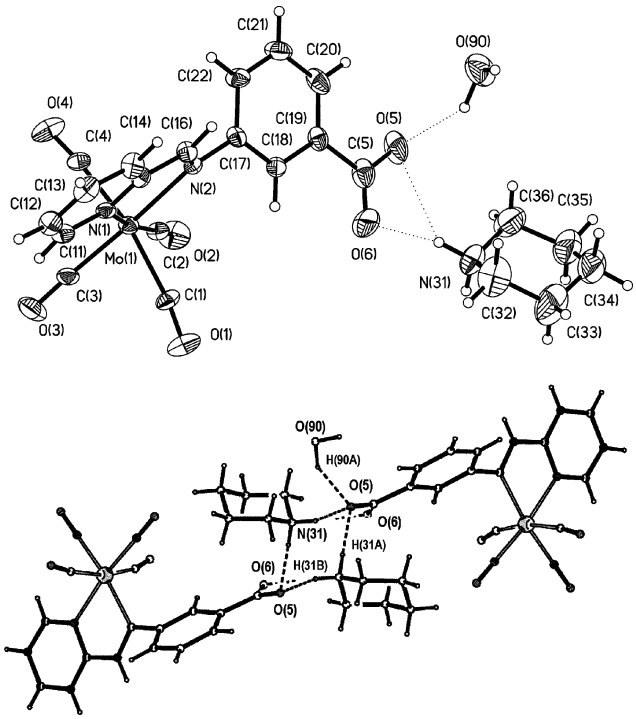
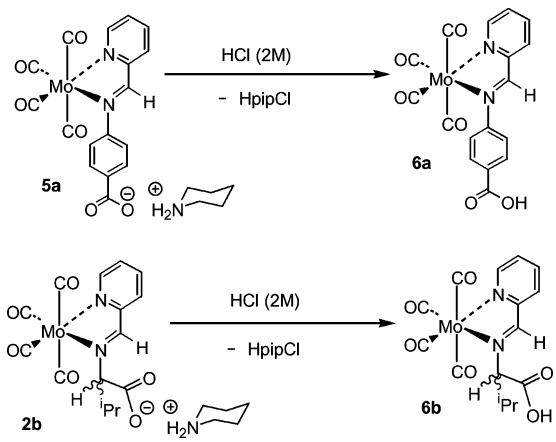


Fig. 7 Perspective view of compound **5b** showing the atom numbering (above) and ion pair dimerization by hydrogen bonding (below). Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 2.038(10), Mo(1)–C(2) 1.988(11), Mo(1)–C(3) 1.943(10), Mo(1)–C(4) 2.017(11), Mo(1)–N(1) 2.236(7), Mo(1)–N(2) 2.245(7), C(5)–O(5) 1.261(16), C(5)–O(6) 1.195(17), C(4)–Mo(1)–C(1) 168.3(4), C(3)–Mo(1)–N(2) 172.0(3), C(2)–Mo(1)–N(1) 172.0(3), N(2)–Mo(1)–N(1) 72.4(3), O(5)–C(5)–O(6) 124.1(12). Hydrogen bonds: H(90A)···O(5) 1.965(13), O(90)–H(90A)···O(5) 144.89(6), H(31A)···O(5) 1.897(12), N(31)–H(31A)···O(5) 177.21(3), H(31B)···O(6) 1.898(10), N(31)–H(31B)···O(6) 162.60(5), H(31B)···O(5) 2.481(12), N(31)–H(31B)···O(5) 138.64(5).



Scheme 6

Experimental

Materials and general methods

All operations were performed under an atmosphere of dry dinitrogen using Schlenk and vacuum techniques. Details of the instrumentation and experimental procedures have been given elsewhere.[18] Literature procedures for the preparation of starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated.

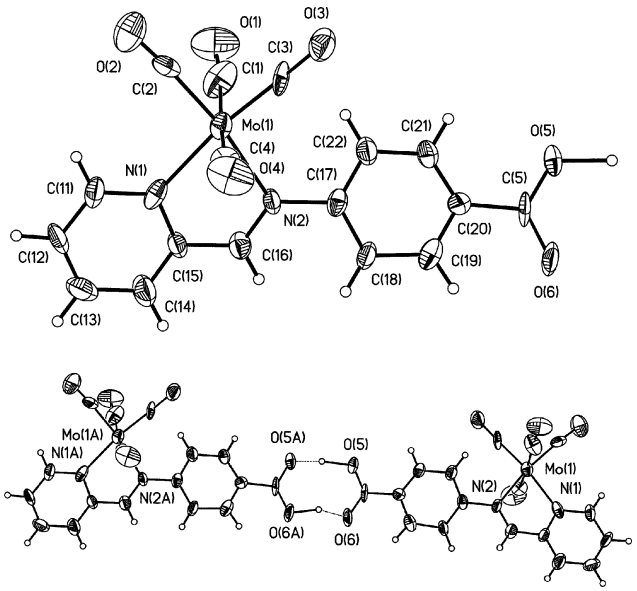


Fig. 8 Perspective view of compound **6a** showing the atom numbering (above) and ion pair dimerization by hydrogen bonding (below). Selected bond lengths (Å) and angles (°): Mo(1)–C(1) 1.80(3), Mo(1)–C(2) 1.89(2), Mo(1)–C(3) 1.729(19), Mo(1)–C(4) 1.96(2), Mo(1)–N(1) 2.180(15), Mo(1)–N(2) 2.250(14), C(5)–O(5) 1.25(2), C(5)–O(6) 1.22(2); C(1)–Mo(1)–C(4) 169.0(9), C(2)–Mo(1)–N(2) 170.8(8), C(3)–Mo(1)–N(1) 172.0(6), N(2)–Mo(1)–N(1) 71.1(5), O(6)–C(5)–O(5) 121.9(15). Hydrogen bonds: H(5)···O(5) 1.296(9), O(5)···H(5)···O(5) 172.86(10), H(6)···O(6) 1.256(10), O(6)···H(6)···O(6) 158.63(10).

Complexes

[Mo(CO)$_4$(py-2-C(H)=NCH$_2$COOEt)] (1). To a solution of pyridine-2-carbaldehyde (0.085 g, 0794 mmol) and [H$_3$NCH$_2$-COOEt]Cl (0.111 g, 0.794 mmol) in ethanol (20 cm^3) was added [Mo(CO)$_4$(pip)$_2$] (0.3 g, 0.794 mmol), and the mixture was heated at 50 °C, with stirring, for 30 min. The color changed quickly from yellow to dark purple. The solvents were evaporated *in vacuo*, and the residue was washed with hexane (2 × 15 cm^3), and then extracted repeatedly with Et$_2$O. The collected extracts were filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound **1** as black microcrystals. Yield 0.196 g (62%). Anal. Calc. for C$_{14}$H$_{12}$MoN$_2$O$_6$: C 42.02, H 3.02, N 7.00. Found: C 42.37, H 2.80, N 6.82%. IR (CH$_2$Cl$_2$), *ν*(CO): 2017 s, 1912 vs, 1888 (sh), 1841 s, cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 9.12 [d (5 Hz), 1H, H^6 of py], 8.49 [s, 1H, py-C(*H*)=N], 7.92 [m, 1H, H^4 of py], 7.80 [d (7 Hz), 1H, H^3 of py], 7.44 [m, 1H, H^5 of py], 4.85 [s, 2H, NC*H*$_2$COOEt], 4.34 [q (7 Hz), 2H, OC*H*$_2$CH$_3$], 1.37 [t (7 Hz), 3H, OCH$_2$C*H*$_3$] ppm.

General preparation of complexes derived from α-amino acids [Hpip][Mo(CO)$_4${py-2-C(H)=NCH(R)COO}] (2a,b). A suspension of the amino acid (0.794 mmol) and pyridine-2-carbaldehyde (0.085 g, 0794 mmol) in EtOH (20 cm^3) was stirred at 50 °C for 10 min. To this was added [Mo(CO)$_4$(pip)$_2$] (0.3 g, 0.794 mmol), and the mixture was heated at 50 °C, with stirring, for 15 min. The color changed quickly from yellow to dark purple. The solvents were evaporated *in vacuo*, and the residue was washed with hexane (2 × 15 cm^3), and then extracted with Et$_2$O to separate the neutral decarboxylation products **3** (see below). The resulting solid residue was dissolved in CH$_2$Cl$_2$ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compounds **2** as red–black microcrystals.

2a. Yield 0.22 g (59%). Anal. Calc. for C$_{18}$H$_{21}$MoN$_3$O$_6$: C 45.87, H 4.49, N 8.92. Found: C 46.07, H 4.65, N 8.89%. IR (CH$_2$Cl$_2$), *ν*(CO): 2014 s, 1906 vs, 1880 (sh), 1830 s, cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 9.09 [d (5 Hz), 1H, H^6 of py], 8.63 [s, 1H, py-C(*H*)=N], 7.88 [m, 1H, H^4 of py], 7.73 [d (8 Hz), 1H, H^3 of py], 7.37 [m, 1H, H^5 of py], 4.64 [q (7 Hz), 1H, NCHCOO], 3.10–1.26 [m (br), 10H, CH$_2$ of Hpip], 1.73 [d (7 Hz), 3H, CHC*H*$_3$] ppm.

2b. Yield 0.29 g (73%). Anal. Calc. for C$_{20}$H$_{25}$MoN$_3$O$_6$: C 48.10, H 5.05, N 8.41. Found: C 48.39, H 4.80, N 8.62%. IR (CH$_2$Cl$_2$), *ν*(CO): 2013 s, 1904 vs, 1881 (sh), 1832 s, cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 9.05 [d (5 Hz), 1H, H^6 of py], 8.84 [s, 1H, py-C(*H*)=N], 7.87 [m, 1H, H^4 of py], 7.73 [d (8 Hz), 1H, H^3 of py], 7.36 [m, 1H, H^5 of py], 4.29 [d (10 Hz), 1H, NCHCOO], 3.10–1.26 [m (br), 10H, CH$_2$ of Hpip], 2.48 [m, 1H, C*H*(CH$_3$)$_2$], 1.09 [d (6 Hz), 3H, CHC*H*$_3$], 0.98 [d (6 Hz), 3H, CHCH$_3$] ppm.

Decarboxylated compounds 3a–c. The ether extracts obtained in the preparation of compounds **2** (see above) were filtered through kieselguhr. Addition of hexane to the filtrate, and slow evaporation gave compounds **3** as red–purple microcrystals.

3a. Yield 0.014 g (5%). Anal. Calc. for C$_{12}$H$_{10}$MoN$_2$O$_4$: C 42.12, H 2.94, N 8.19. Found: C 42.29, H 2.99, N 7.82%. IR (CH$_2$Cl$_2$), *ν*(CO): 2015 s, 1906 vs, 1886 (sh), 1835 s, cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 9.12 [d (5 Hz), 1H, H^6 of py], 8.45 [s, 1H, py-C(*H*)=N], 7.90 [td (7 and 2 Hz), 1H, H^4 of py], 7.72 [d (7 Hz), 1H, H^3 of py], 7.40 [m, 1H, H^5 of py], 4.10 [q (7 Hz), 2H, NC*H*$_2$], 1.59 [t (7 Hz), 3H, NCH$_2$C*H*$_3$] ppm.

3b. Yield 0.018 g (6%). Anal. Calc. for C$_{14}$H$_{14}$MoN$_2$O$_4$: C 45.42, H 3.81, N 7.57. Found: C 45.18, H 3.63, N 7.87%. IR (CH$_2$Cl$_2$), *ν*(CO): 2015 s, 1907 vs, 1886 (sh), 1836 s, cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 9.11 [d (6 Hz), 1H, H^6 of py], 8.35 [s, 1H, py-C(*H*)=N], 7.91 [td (7 and 1 Hz), 1H, H^4 of py], 7.73 [d (7 Hz), 1H, H^3 of py], 7.41 [m, 1H, H^5 of py], 3.82 [m, 2H, NCH$_2$], 2.65 [m, 1H, C*H*(CH$_3$)$_2$], 0.98 [d (7 Hz), 6H, C*H*(CH$_3$)$_2$] ppm.

3c. Yield 0.20 g (62%). Anal. Calc. for C$_{17}$H$_{12}$MoN$_2$O$_4$: C 50.51, H 2.99, N 6.93. Found: C 50.38, H 2.90, N 6.81%. IR (CH$_2$Cl$_2$), *ν*(CO): 2016 s, 1910 vs, 1886 (sh), 1837 s, cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 9.09 [d (5 Hz), 1H, H^6 of py], 8.46 [s, 1H, py-C(*H*)=N], 7.88 [m, 1H, H^4 of py], 7.73 [d (7 Hz), 1H, H^3 of py], 7.40 [m, 6H, H^5 of py and C$_6$H$_5$], 5.24 [s, 2H, NCH$_2$] ppm.

[Hpip][Mo(CO)$_4${py-2-C(H)=NCH$_2$CH$_2$COO}] (4). A suspension of β-alanine (0.071 g, 0.79 mmol) and pyridine-2-carbaldehyde (0.085 g, 0794 mmol), in ethanol (20 cm^3) was stirred at 50 °C for 10 min. Then [Mo(CO)$_4$(pip)$_2$] (0.3 g, 0.794 mmol) was added, and the mixture was stirred at 50 °C for 35 min. The color changed quickly from yellow to dark purple. The solvents were evaporated *in vacuo*, and the residue was washed with hexane and Et$_2$O. The resulting solid residue was dissolved in CH$_2$Cl$_2$ and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compound **4** as red microcrystals. Yield 0.26 g (71%). Anal. Calc. for C$_{18}$H$_{21}$MoN$_3$O$_6$: C 45.87, H 4.49, N 8.92. Found: C 45.66, H 4.26, N 7.71%. IR (CH$_2$Cl$_2$), *ν*(CO): 2015 s, 1907 vs, 1883 (sh), 1836 s, cm^{-1}. ^{1}H NMR (CDCl$_3$): *δ* 9.07 [d (5 Hz), 1H, H^6 of py], 8.58 [s, 1H, py-C(*H*)=N], 7.89 [m, 1H, H^4 of py], 7.72 [d (8 Hz), 1H, H^3 of py], 7.39 [m,

1H, H^5 of py], 4.25 [t (7 Hz), 2H, NCH_2CH_2], 2.90 [t (7 Hz), 2H, CH_2CH_2COO], 3.10–1.26 [m (br), 10H, CH_2 of Hpip] ppm.

[Hpip][Mo(CO)$_4${py-2-C(H)=NC$_6$H$_4$(COO)-4}] (5a) and [Hpip]-[Mo(CO)$_4${py-2-C(H)=NC$_6$H$_4$(COO)-3}] (5b). A suspension of the appropriate aminobenzoic acid (0.794 mmol), pyridine-2-carbaldehyde (0.085 g, 0794 mmol) and [Mo(CO)$_4$(pip)$_2$] (0.3 g, 0.794 mmol) in EtOH (20 cm^3) was stirred at room temperature for 3 h (for **5a**) or 1 h (for **5b**). Then the solution was warmed gently to ensure complete reaction. The color changed from yellow to dark violet. The solvents were evaporated *in vacuo*, and the residue was washed with hexane (2 × 15 cm^3) and Et_2O (10 cm^3). The resulting solid residue was dissolved in CH_2Cl_2 and filtered through kieselguhr. Addition of hexane and slow evaporation at reduced pressure gave compounds **5a,b** as dark purple microcrystals.

5a. Yield 0.313 g (76%). Anal. Calc. for $C_{22}H_{21}MoN_3O_6$: C 50.88, H 4.08, N 8.09. Found: C 50.46, H 4.26, N 7.65%. IR (CH_2Cl_2), ν(CO): 2016 s, 1911 vs, 1890 (sh), 1842 s, cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.21 [d (6 Hz), 1H, H^6 of py], 8.57 [s, 1H, py-C(H)=N], 8.16 [d (8 Hz), 2H, H^2 and H^6 of Ph], 7.90 [m, 2H, H^3 of py and H^4 of py], 7.48 [m, 3H, H^5 of py, H^3 of Ph and H^5 of Ph], 3.10–1.26 [m (br), 10H, CH_2 of Hpip] ppm.

5b. Yield 0.334 g (81%). Anal. Calc. for $C_{22}H_{21}MoN_3O_6$: C 50.88, H 4.08, N 8.09. Found: C 51.19, H 4.38, N 7.95%. IR (CH_2Cl_2), ν(CO): 2016 s, 1911 vs, 1890 (sh), 1841 s, cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.19 [d (5 Hz), 1H, H^6 of py], 8.62 [s, 1H, py-C(H)=N], 8.07 [m, 2H, H^2 and H^6 of Ph, signals overlap], 7.95 [td (8 and 1 Hz), 1H, H^4 of py], 7.85 [d (8 Hz), 1H, H^3 of py], 7.69 [d (8 Hz), 1H, H^4 of Ph], 7.49 [m, 2H, H^5 of Ph and H^5 of py, signals overlap], 3.10 to 1.26 [m (br), 10H, CH_2 of Hpip] ppm.

[Mo(CO)$_4${py-2-C(H)=NC$_6$H$_4$-COOH-4}] (6a) and [Mo(CO)$_4$-{py-2-C(H)=NCH(CH(CH$_3$)$_2$)COOH}] (6b). A stirred solution of compound **2b** (0.1 g, 0.200 mmol) or compound **5a** (0.1 g, 0.192 mmol) in CH_2Cl_2 was washed with 2 M HCl (3 × 10 cm^3) and then water (2 × 15 cm^3). The solution was dried with magnesium sulfate and filtered through kieselguhr. The solvents were evaporated *in vacuo*, and the residue was washed with hexane (2 × 15 cm^3) and Et_2O (2 × 5 cm^3). The resulting solid residue was dissolved in CH_2Cl_2. Addition of hexane and slow evaporation at reduced pressure gave compounds **6** as dark red (**6a**) or black (**6b**) microcrystals.

6a. Yield 0.070 g (84%). Anal. Calc. for $C_{17}H_{10}MoN_2O_6$: C 47.02, H 2.32, N 6.45. Found: C 47.25, H 2.63, N 6.21%. IR (CH_2Cl_2), ν(CO): 2017 s, 1914 vs, 1893 (sh), 1845 s, cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.23 [d (6 Hz), 1H, H^6 of py], 8.60 [s, 1H, py-C(H)=N], 8.24 [d (8 Hz), 2H, H^2 and H^6 of Ph], 7.94 [m, 2H, H^3 of py and H^4 of py], 7.54 [m, 3H, H^5 of py, H^3 of Ph and H^5 of Ph] ppm.

6b. Yield 0.065 g (79%). Anal. Calc. for $C_{15}H_{14}MoN_2O_6$: C 43.49, H 3.41, N 6.76. Found: C 43.89, H 3.89, N 6.65%. IR (CH_2Cl_2), ν(CO): 2016 s, 1909 vs, 1888 (sh), 1838 s, cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.12 [d (5 Hz), 1H, H^6 of py], 8.65 [s, 1H, py-C(H)=N], 7.94 [m, 1H, H^4 of py], 7.82 [d (8 Hz), 1H, H^3 of py], 7.44 [m, 1H, H^5 of py], 4.36 [d (7 Hz), 1H, NCH], 2.71 [m, 1H, CH(CH$_3$)$_2$], 1.16 [d (6 Hz), 3H, CHCH_3], 1.00 [d (6 Hz), 3H, CHCH_3] ppm.

X-Ray diffraction study of 1, 2a, 3b, 3c, 4, 5a, 5b and 6a

Crystals were grown by slow diffusion of hexane into concentrated solutions of the complexes in CH_2Cl_2 at −20 °C. Intensity measurement was made with a Bruker AXS SMART 1000 diffractometer with graphite-monochromated Mo-Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space (full sphere for **2a**) was collected up to $2\theta = 48.6°$. Raw frame data were integrated with the SAINT[19] program. A semi-empirical absorption correction was applied with the program SADABS.[20] The structures were solved by direct methods with SIR2002,[21] under WINGX,[22] and refined against F^2 with SHELXTL.[23] All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Calculations and graphics were made with SHELXTL and PARST,[24] and graphics were made with SHELXTL. Crystal data, particular details and CCDC reference numbers are given below for each structure.

Compound 1. $C_{14}H_{12}MoN_2O_6$, $M = 400.20$, monoclinic, space group = $P2_1/c$, $a = 7.311(5)$, $b = 16.795(10)$, $c = 12.823(8)$ Å, $\beta = 91.026(10)°$, $U = 1574(2)$ Å^3, $T = 296(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.865 mm^{-1}, 7056 reflections collected, 2259 unique ($R_{int} = 0.0378$), $R_1 = 0.0271$, $wR_2 = 0.0522$. CCDC 281340.

Compound 2a. $C_{18}H_{21}MoN_3O_6$, $M = 471.32$, triclinic, space group = $P1$, $a = 9.094(3)$, $b = 10.836(3)$, $c = 12.111(4)$ Å, $\alpha = 91.259(5)$, $\beta = 109.767(5)$, $\gamma = 109.143(4)°$, $U = 1049.0(5)$ Å^3, $T = 296(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.662 mm^{-1}, 6870 reflections collected, 5785 unique ($R_{int} = 0.0204$), $R_1 = 0.0509$, $wR_2 = 0.1427$. The choice of the chiral space group $P1$ was suggested by the XPREP subroutine of SHELXTL on the basis of the value of the mean $|EE^{*-1}| = 0.795$. The Flack parameter was refined with the instruction TWIN, and converged to 0.42(7), indicating the presence of two enantiomers in the lattice. Alternatively, the structure was solved and refined on the centrosymmetric space group $P\bar{1}$. However this lead to poorer results. Apart from the expectable disorder in the α-carbon of the amino acid, it was found that all the atoms of the piperidinium cation were also heavily disordered, with very high temperature factors. Several attempts to model the disorder led to no better results than those obtained with the non-centrosymmetric space group. CCDC 281341.

Compound 3b. $C_{14}H_{14}MoN_2O_4$, $M = 370.21$, monoclinic, space group = $P2_1/c$, $a = 6.655(1)$, $b = 15.676(3)$, $c = 15.454(3)$ Å, $\beta = 99.916(4)°$, $U = 1588.2(5)$ Å^3, $T = 296(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.841 mm^{-1}, 6971 reflections collected, 2288 unique ($R_{int} = 0.0325$), $R_1 = 0.0336$, $wR_2 = 0.0876$. CCDC 281342.

Compound 3c. $C_{17}H_{12}MoN_2O_4$, $M = 404.23$, monoclinic, space group = $P2_1/n$, $a = 10.401(1)$, $b = 15.754(2)$, $c = 10.818(1)$ Å, $\beta = 108.019(2)°$, $U = 1685.8(4)$ Å^3, $T = 299(2)$ K, $Z = 4$, μ(Mo-Kα) = 0.800 mm^{-1}, 10821 reflections collected, 2418 unique ($R_{int} = 0.0370$), $R_1 = 0.0251$, $wR_2 = 0.0560$. CCDC 281343.

Compound 4. $C_{18}H_{21}MoN_3O_6$, $M = 471.32$, monoclinic, space group = $C2/c$, $a = 17.481(8)$, $b = 11.553(6)$, $c = 20.934(10)$ Å, $\beta = 98.40(2)°$, $U = 4182(4)$ Å^3, $T = 293(2)$ K, $Z = 8$, μ(Mo-Kα) = 0.664 mm^{-1}, 9331 reflections collected, 3065 unique ($R_{int} = 0.0270$), $R_1 = 0.0349$, $wR_2 = 0.0984$. CCDC 281344.

Compound 5a. $C_{22}H_{21}MoN_3O_6$, $M = 519.36$, triclinic, space group = $P\bar{1}$, $a = 6.654(1)$, $b = 8.374(2)$, $c = 21.538(4)$ Å, $\alpha = 86.669(3)$, $\beta = 87.253(3)$, $\gamma = 69.782(4)°$, $U = 1123.8(4)$ Å^3, $T = 293(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.626 mm^{-1}, 4981 reflections collected, 3207 unique ($R_{int} = 0.0134$), $R_1 = 0.0253$, $wR_2 = 0.0802$. CCDC 281345.

Compound 5b. $C_{22}H_{21}MoN_3O_6 \cdot 0.3H_2O$, $M = 524.76$, monoclinic, space group = $C2/c$, $a = 15.710(6)$, $b = 6.746(3)$, $c = 43.915(17)$ Å, $\beta = 90.260(6)°$, $U = 4654(3)$ Å^3, $T = 293(2)$ K, $Z = 8$, μ(Mo-Kα) = 0.607 mm^{-1}, 9975 reflections collected, 3357 unique ($R_{int} = 0.0505$), $R_1 = 0.0808$, $wR_2 = 0.1896$. A peak lying on a twofold axis was found to correspond to a disordered molecule of water. The occupancy was refined to a value of 0.3. CCDC 281346.

Compound 6a. $C_{17}H_{10}MoN_2O_6 \cdot 0.1CH_2Cl_2$, $M = 442.70$, monoclinic, space group = $C2/c$, $a = 24.17(3)$, $b = 10.648(11)$, $c = 16.561(17)$ Å, $\beta = 102.79(2)°$, $U = 4156(8)$ Å^3, $T = 296(2)$ K, $Z = 8$, μ(Mo-Kα) = 0.688 mm^{-1}, 9235 reflections collected, 3007 unique ($R_{int} = 0.0902$), $R_1 = 0.0871$, $wR2 = 0.2065$. Several peaks were found near to an inversion centre, and were modelled as a low occupancy (0.1) molecule of dichloromethane which was refined as a rigid group with a common isotropic temperature factor for Cl and C atoms. CCDC 281347.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511637f

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References

1 (*a*) K. K. W. Lo, W. K. Hui and D. C. M. Ng, *J. Am. Chem. Soc.*, 2002, **124**, 9344; (*b*) M. K. Brennaman, J. H. Alstrum-Acevedo, C. N. Fleming, P. Jang, T. J. Meyer and J. M. Papanikolas, *J. Am. Chem. Soc.*, 2002, **124**, 15094.
2 (*a*) K. A. Stephenson, J. Zubieta, S. R. Bannerjee, M. K. Levadala, L. Taggart, L. Ryan, N. McFarlane, D. R. Boreham, K. P. Maresca, J. W. Babich and J. F. Valliant, *Bioconjugate Chem.*, 2004, **15**, 128; (*b*) M. B. Skaddan, F. R. Wüst, S. Jonson, R. Syhre, M. J. Welch, H. Spies and J. Katzenellenbogen, *Nucl. Med. Biol.*, 2000, **27**, 269; (*c*) J. Zhang, J. J. Vittal, W. Henderson, J. R. Wheaton, I. H. Hall, T. S. A. Hor and Y. K. Yan, *J. Organomet. Chem.*, 2002, **650**, 123.
3 (*a*) L. Pu, *Chem. Rev.*, 2004, **104**, 1687; (*b*) J. Wald, R. Alberto, K. Ortner and L. Candreia, *Angew. Chem., Int. Ed.*, 2001, **40**, 3062.
4 (*a*) R. N. Patel, N. Singh and K. K. Shukla, *J. Inorg. Biochem.*, 2005, **99**, 651; (*b*) M. H. Schifeld and D. Y. Chung, *J. Inorg. Biochem.*, 2004, **96**, 226; (*c*) M. Merkel and D. Schiedens, *Eur. J. Inorg. Chem.*, 2004, 783; (*d*) T. Humphry, M. Forconi, N. H. Williams and A. C. Hengge, *J. Am. Chem. Soc.*, 2002, **124**, 14860.
5 (*a*) R. Mejía-Rodríguez, D. Chong, J. H. Reibenspies, M. P. Soriaga and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2004, **126**, 12004; (*b*) F. Gloaguen, J. D. Lawrence, M. Schmidt, S. R. Wilson and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 2001, **123**, 12518; (*c*) S. J. George, Z. Cui, M. Razavet and C. J. Pickett, *Chem. Eur. J.*, 2002, **8**, 4037.
6 (*a*) D. R. Van Staveren, E. Bothe and N. Metzler-Nolte, *Organometallics*, 2003, **22**, 3102; (*b*) D. R. Van Staveren, E. Bill, E. Bothe, M. Bühl, T. Weyhermüller and N. Metzler-Nolte, *Chem. Eur. J.*, 2002, **8**, 1649; (*c*) D. R. Van Staveren, T. Weyhermüller and N. Metzler-Nolte, *Organometallics*, 2000, **19**, 3730.
7 B. Galán, D. Miguel, J. Pérez and V. Riera, *Organometallics*, 2002, **21**, 2979.
8 J. Pérez, V. Riera, A. Rodríguez and D. Miguel, *Organometallics*, 2002, **21**, 5437.
9 R. S. Herrick, K. L. Houde, J. S. McDowell, L. P. Kizeck and G. Bonavia, *J. Organomet. Chem.*, 1999, **589**, 29.
10 R. S. Herrick, C. J. Ziegler, H. Bohan, M. Corey, M. Eskander, J. Giguere, N. McMicken and I. Wrona, *J. Organomet. Chem.*, 2003, **687**, 178.
11 R. S. Herrick, I. Wrona, N. McMicken, G. Jones, C. J. Ziegler and J. Shaw, *J. Organomet. Chem.*, 2004, **689**, 4848.
12 D. J. Darensbourg and R. L. Kump, *Inorg. Chem.*, 1978, **17**, 2680.
13 R. D. Bach and C. Canepa, *J. Am. Chem. Soc.*, 1997, **119**, 11725.
14 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; D. Braga, F. Grepioni and G. R. Desiraju, *J. Organomet. Chem.*, 1997, **548**, 33.
15 G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.
16 G. R. Desiraju, *Chem. Commun.*, 1997, 1475.
17 G. R. Desiraju and C. V. K. Sharma, *J. Chem. Soc., Chem. Commun.*, 1991, 1239.
18 G. Barrado, M. M. Hricko, D. Miguel, V. Riera, H. Wally and S. García-Granda, *Organometallics*, 1998, **17**, 820.
19 *SAINT+: SAX area detector integration program. Version 6.02*. Bruker AXS, Inc., Madison, WI, 1999.
20 G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*, University of Göttingen: Göttingen, Germany, 1997.
21 M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidory and R. Spagna, *SIR2002, A program for automatic solution and refinement of crystal structures*; A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
22 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
23 G. M. Sheldrick, *SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data. Version 5.1*. Bruker AXS, Inc. Madison, WI, 1998.
24 (*a*) M. Nardelli, *Comput. Chem.*, 1983, **7**, 95–97; (*b*) M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659.