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Synthesis and characterisation of molybdenum complexes bearing highly functionalised imido substituents†

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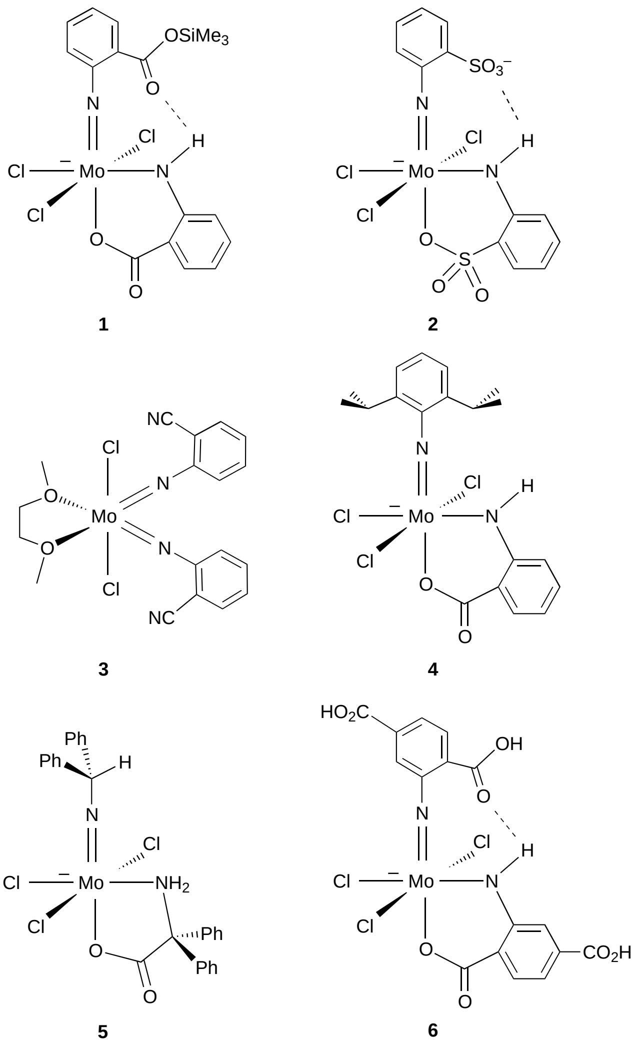
The monofunctionalised anilines 2-$(H_2N)C_6H_4X$ (where X = CO_2H, SO_3H, or CN) reacted with sodium molybdate in the presence of NEt_3 and $SiMe_3Cl$ in refluxing dme (1,2-dimethoxyethane) to give $[NEt_3H][MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}\{2\text{-}Me_3SiO_2CC_6H_4N\}]$ **1**, $[NEt_3H]_2[MoCl_3\{2\text{-}NC_6H_4SO_3\}\{2\text{-}(HN)C_6H_4SO_3\}]$ **2** and $[MoCl_2(2\text{-}NCC_6H_4N)_2(dme)]$ **3**. Treatment of sodium molybdate with anthranilic acid and 2,6-$Pr^i{}_2C_6H_3NH_2$ in a 1:1 ratio afforded $[NEt_3H][MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}(NC_6H_3Pr^i{}_2\text{-}2,6)]$ **4**. Products of reactions of sodium molybdate with the amino acid 2,2-diphenylglycine and 2-aminoterephthalic acid, namely $[NEt_3H][MoCl_3(NCHPh_2)(H_2NCPh_2CO_2)]$ **5** and $[NEt_3H][MoCl_3\{2\text{-}HNC_6H_3CO_2(CO_2H)\text{-}1,4\}\{2\text{-}NC_6H_3(CO_2H)_2\text{-}1,4\}]$ **6** respectively are also reported. Complexes **1** to **6** have been structurally characterised; all contain pseudo-octahedral geometries about the metal centre, and all except **3** are salts in which the anion contains a *mer* arrangement of chloride ligands.

The reaction of ammonium[1] or sodium[2] molybdate with amines or anilines in the presence of trimethylsilyl chloride and a sacrificial base (typically triethylamine) is commonly utilised as a convenient ‘one pot’ entry into bis(imido)molybdenum chemistry. Schrock and co-workers[3] have shown that the methodology may be extended to arylimido complexes bearing functionalities such as Br, CF_3 and CN (*para* position). We became interested in establishing whether or not the molybdate reaction conditions could also be applied to the synthesis of imido complexes bearing highly functional substituents, *e.g.* CO_2H and SO_3H, groups that ordinarily would also be expected to get involved in metal complexation. Here, we describe a series of products (Scheme 1) arising from treatment of sodium molybdate with functionalised anilines all of which bear molybdenum-bound imido groups. Crystal structure analyses of the products have facilitated an understanding of the coordination patterns arising in these highly functionalised imido species. These results encouraged us to try an amino acid under the molybdate preparation conditions and a yet more highly functionalised aniline, containing two carboxylic acid substituents. The products from these reactions have also been structurally characterised. A number of organoimidorhenium(V) complexes containing a ligand derived from glycine have recently been reported.[4] The only other example of an organoimido group functionalised with a carboxylic acid group is the rather poorly characterised $[ReCl(OEt)(PPh_3)_2(NC_6H_4CO_2)]$.[5]



Scheme 1

Results and Discussion

2-$(H_2N)C_6H_4X$ derivatives

The reaction of Na_2MoO_4 with 2 equivalents of anthranilic acid, 2-$(H_2N)C_6H_4CO_2H$, in the presence of NEt_3 and $SiMe_3Cl$ in refluxing dme (1,2-dimethoxyethane) afford after work-up the highly crystalline salt $[NEt_3H][MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}\{2\text{-}Me_3SiO_2CC_6H_4N\}]$ **1**, in 27% isolated yield. A structural representation of the anion in **1** is shown in Scheme 1. Crystals suitable for an X-ray study were grown from acetonitrile. Fig. 1 shows the *mer*-trichloro pseudo-octahedral geometry of **1**; bond lengths and angles are collected in Table 1. The main distortion arises from the bite angle of the chelating amidobenzoate ligand [81.81(14)°]. A *trans* influence is exerted by the amido ligand, Mo–Cl(2) 2.4214(12) Å; the mutually *trans* Mo–Cl distances are

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† Dedicated to the memory of Professor Sir Geoffrey Wilkinson.

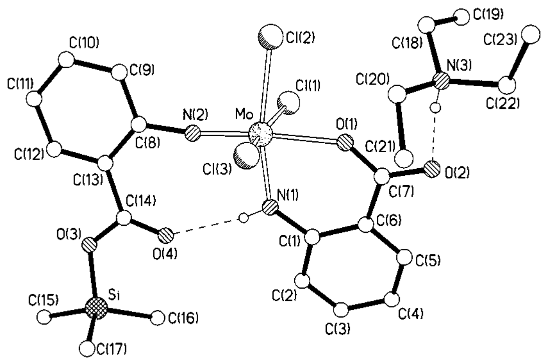


Fig. 1 Molecular structure of complex **1**, without C–H hydrogen atoms and showing hydrogen bonding

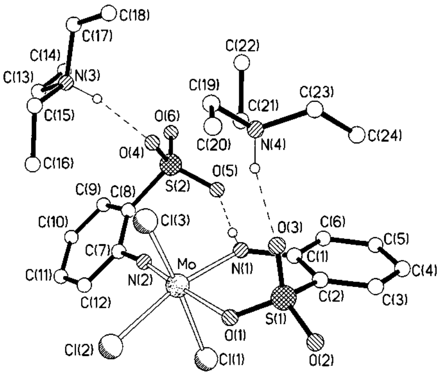


Fig. 2 Molecular structure of complex **2**; details as in Fig. 1

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Mo–N(1)	1.929(4)	Mo–O(1)	2.113(3)
Mo–N(2)	1.728(4)	Mo–Cl(1)	2.4045(14)
Mo–Cl(2)	2.4214(12)	Mo–Cl(3)	2.4025(13)
N(1)–C(1)	1.376(6)	C(7)–O(2)	1.242(5)
C(7)–O(1)	1.278(5)	N(2)–C(8)	1.390(5)
C(14)–O(4)	1.208(6)	C(14)–O(3)	1.332(5)
N(2)–Mo–N(1)	94.4(2)	N(2)–Mo–O(1)	175.1(2)
N(1)–Mo–O(1)	81.84(14)	N(2)–Mo–Cl(3)	92.98(13)
N(1)–Mo–Cl(3)	98.38(13)	O(1)–Mo–Cl(3)	84.49(9)
N(2)–Mo–Cl(1)	97.46(13)	N(1)–Mo–Cl(1)	89.31(13)
O(1)–Mo–Cl(1)	85.68(10)	Cl(3)–Mo–Cl(1)	166.53(4)
N(2)–Mo–Cl(2)	97.69(12)	N(1)–Mo–Cl(2)	166.69(12)
O(1)–Mo–Cl(2)	86.37(9)	Cl(3)–Mo–Cl(2)	86.55(4)
Cl(1)–Mo–Cl(2)	83.65(5)	C(1)–N(1)–Mo	135.8(3)
C(7)–O(1)–Mo	135.9(3)	C(8)–N(2)–Mo	170.6(3)

ca. 0.02 Å shorter. The carboxylate group of this chelating ligand is *trans* to a near-linear imido group, Mo–N(2)–C(8) 170.6(3)°, which is acting as a four-electron (neutral) donor [Mo–N(2) 1.728(4) Å]. Interestingly, the *ortho*-acid group of this organoimido ligand has been attacked by $SiMe_3Cl$ resulting in the formation of a silyl ester group. There is hydrogen bonding between the O(4) atom of the silyl ester group and the amide proton of the amidobenzoate chelate, and also between the cation Et_3NH^+ and O(2) of the chelating ligand.

A similar reaction of Na_2MoO_4 with the sulfonic acid 2-$(H_2N)C_6H_4SO_3H$ in refluxing dme afforded after work-up large red needles in 36% isolated yield. Spectroscopic data on this product **2** were not consistent with a simple bis(imido)molybdenum type complex, and hence its structure was determined by X-ray diffraction. The structure is shown in Fig. 2 and a representation of the anionic component is depicted in Scheme 1. Selected bond lengths and angles are given in Table 2. Again the molecule has a very similar pseudo-octahedral geometry with a chelating amidobenzenesulfonate type ligand and a *mer* configuration of chlorines all of which are mutually *cis* to the organoimido function. In contrast to **1**, the *ortho*-acid group on the imido ligand has not been attacked by $SiMe_3Cl$ and retains a uninegative charge. There are hydrogen bonds from both cations and from the N–H group of the chelating ligand to sulfonate oxygen atoms.

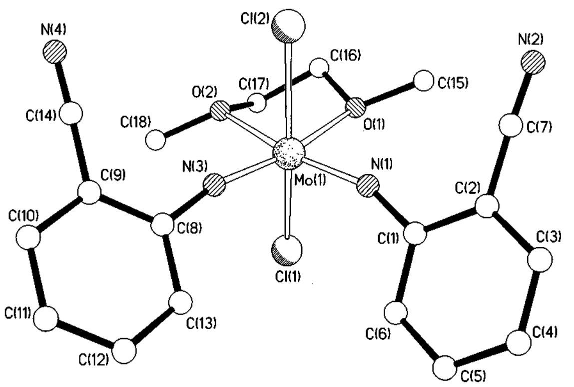


Fig. 3 Molecular structure of complex **3**; details as in Fig. 1

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Mo–N(1)	1.943(3)	Mo–O(1)	2.177(3)
Mo–N(2)	1.717(3)	Mo–Cl(1)	2.4153(11)
Mo–Cl(2)	2.4198(10)	Mo–Cl(3)	2.3725(11)
N(1)–C(1)	1.397(5)	S(1)–O(1)	1.484(3)
S(1)–O(2)	1.436(3)	S(1)–O(3)	1.446(3)
N(2)–C(7)	1.390(5)	S(2)–O(4)	1.459(3)
S(2)–O(5)	1.458(3)	S(2)–O(6)	1.436(3)
N(2)–Mo–N(1)	93.67(15)	N(2)–Mo–O(1)	175.56(13)
N(1)–Mo–O(1)	82.57(12)	N(2)–Mo–Cl(3)	96.25(11)
N(1)–Mo–Cl(3)	98.35(11)	O(1)–Mo–Cl(3)	86.67(8)
N(2)–Mo–Cl(1)	93.48(11)	N(1)–Mo–Cl(1)	89.00(11)
O(1)–Mo–Cl(1)	84.12(8)	Cl(3)–Mo–Cl(1)	167.39(4)
N(2)–Mo–Cl(2)	99.35(11)	N(1)–Mo–Cl(2)	165.68(11)
O(1)–Mo–Cl(2)	84.16(7)	Cl(3)–Mo–Cl(2)	86.19(4)
Cl(1)–Mo–Cl(2)	84.32(4)	C(1)–N(1)–Mo	138.1(3)
S(1)–O(1)–Mo	131.9(2)	C(7)–N(2)–Mo	171.3(3)

Treatment of Na_2MoO_4 with 2-cyanoaniline at 80 °C in MeCN affords after work-up the bis(imido)molybdenum product $[MoCl_2(2\text{-}NCC_6H_4N)_2(dme)]$ **3**. The structure of one of the two crystallographically independent molecules of **3** is shown in Fig. 3; important bond lengths and angles are given in Table 3. The molecular geometry is octahedral with *trans* chlorines and *cis* imido groups. The N(1)–Mo(1)–N(3) angle is opened up to 104.1(2)° and the Cl(1)–Mo(1)–Cl(2) angle is reduced to 159.71(5)° from ideal octahedral values. The four Mo–N distances for the two molecules are all approximately equal at 1.736(4)–1.752(4) Å, but the range of Mo–N–C angles [155.2(3) to 169.8(3)°] reflects the ready deviation of this angle from linearity. Clearly, the *ortho*-cyano groups do not interact with the metal centre in any way.

The simultaneous addition of the two amines 2-$(H_2N)C_6H_4CO_2H$ and $2,6\text{-Pr}^i_2C_6H_3NH_2$ to a stirred suspension of Na_2MoO_4 in dme under similar conditions affords after work-up the highly crystalline salt $[NEt_3H][MoCl_3\{2\text{-}(HN)C_6H_4CO_2\}(NC_6H_3Pr^i_2\text{-}2,6)]$ **4** in good yield. The IR and NMR data (see Experimental section) are consistent with this formulation. Crystals suitable for an X-ray study were grown from acetonitrile. Fig. 4 depicts the *mer*-trichloro pseudo-octahedral geometry of **4** (see Scheme 1 for a simplified structural representation of the anion). Bond lengths and angles are collected in Table 4. The main distortion arises from the bite angle of the chelating amidobenzoate ligand [83.75(9)°]. A *trans* influence is exerted by the amido ligand with Mo–Cl(2) rather longer than the other two Mo–Cl bonds. The carboxylate group

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Mo(1)–N(1)	1.752(4)	Mo(1)–N(3)	1.742(4)
Mo(1)–O(1)	2.312(3)	Mo(1)–O(2)	2.337(3)
Mo(1)–Cl(1)	2.3943(12)	Mo(1)–Cl(2)	2.3864(11)
N(1)–C(1)	1.379(6)	N(3)–C(8)	1.391(5)
Mo(2)–N(5)	1.752(4)	Mo(2)–N(7)	1.736(4)
Mo(2)–O(3)	2.298(3)	Mo(2)–O(4)	2.320(3)
Mo(2)–Cl(3)	2.3846(12)	Mo(2)–Cl(4)	2.4069(12)
N(5)–C(19)	1.385(6)	N(7)–C(26)	1.387(6)
N(3)–Mo(1)–N(1)	104.1(2)	N(3)–Mo(1)–O(1)	164.72(15)
N(1)–Mo(1)–O(1)	91.1(2)	N(3)–Mo(1)–O(2)	94.22(15)
N(1)–Mo(1)–O(2)	161.0(2)	O(1)–Mo(1)–O(2)	70.50(11)
N(3)–Mo(1)–Cl(2)	97.69(13)	N(1)–Mo(1)–Cl(2)	99.93(13)
O(1)–Mo(1)–Cl(2)	80.98(9)	O(2)–Mo(1)–Cl(2)	82.21(9)
N(3)–Mo(1)–Cl(1)	94.30(13)	N(1)–Mo(1)–Cl(1)	92.91(13)
O(1)–Mo(1)–Cl(1)	83.14(9)	O(2)–Mo(1)–Cl(1)	80.63(9)
Cl(2)–Mo(1)–Cl(1)	159.71(5)	C(1)–N(1)–Mo(1)	158.4(3)
C(8)–N(3)–Mo(1)	166.5(3)	N(7)–Mo(2)–N(5)	104.3(2)
N(7)–Mo(2)–O(3)	164.13(14)	N(5)–Mo(2)–O(3)	91.41(15)
N(7)–Mo(2)–O(4)	93.38(14)	N(5)–Mo(2)–O(4)	161.42(15)
O(3)–Mo(2)–O(4)	70.78(11)	N(7)–Mo(2)–Cl(3)	97.85(12)
N(5)–Mo(2)–Cl(3)	100.10(13)	O(3)–Mo(2)–Cl(3)	81.56(10)
O(4)–Mo(2)–Cl(3)	82.96(9)	N(7)–Mo(2)–Cl(4)	94.05(12)
N(5)–Mo(2)–Cl(4)	91.93(13)	O(3)–Mo(2)–Cl(4)	82.75(9)
O(4)–Mo(2)–Cl(4)	80.86(9)	Cl(3)–Mo(2)–Cl(4)	160.42(5)
C(19)–N(5)–Mo(2)	155.2(3)	C(26)–N(7)–Mo(2)	169.8(3)

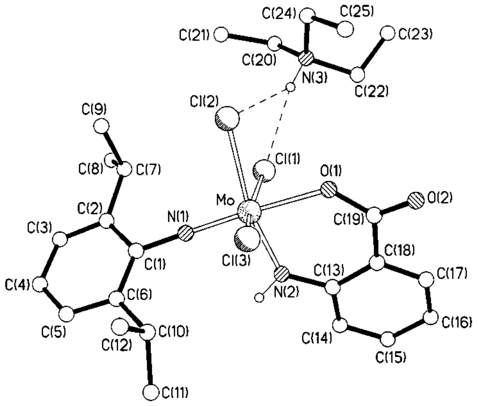


Fig. 4 Molecular structure of complex **4**; details as in Fig. 1

of this chelating ligand is *trans* to a near-linear arylimido group, Mo−N(1)−C(1) 177.8(2)°, which is acting as a four-electron donor [Mo−N(1) 1.740(2) Å]. There is a bifurcated hydrogen bond between the cation Et$_3$NH$^+$ and Cl(1) and Cl(2). Additionally, the anions are linked together in chains by hydrogen bonding between the N−H of the chelate ligand in each anion and carboxylate O(2) of an adjacent anion.

Amino acid derivatives

Treatment of Na$_2$MoO$_4$ with 2,2-diphenylglycine at elevated temperature in dme in the presence of NEt$_3$ and SiMe$_3$Cl affords after work-up large turquoise prisms of complex **5** in good yield. The IR spectrum contains strong stretches in the ν(N−H) and ν(C=O) regions; the ^{1}H NMR spectrum is broad and uninformative. A single-crystal X-ray analysis of **5** reveals an octahedral geometry with meridional chlorines, which are all mutually *cis* to an organoimido ligand (=NCHPh$_2$) derived from decarboxylation of diphenylglycine (Fig. 5, Table 5). A second intact diphenylglycine chelates as an aminocarboxylate to the molybdenum centre and is hydrogen bonded through O(2) to the triethylammonium counter ion.

Table 4 Selected bond lengths (Å) and angles (°) for complex **4**

Mo–N(1)	1.740(2)	Mo–N(2)	1.937(2)
Mo–O(1)	2.099(2)	Mo–Cl(1)	2.4280(8)
Mo–Cl(2)	2.4503(8)	Mo–Cl(3)	2.3837(8)
N(1)–C(1)	1.384(4)	N(2)–C(13)	1.397(3)
C(19)–O(1)	1.283(4)	C(19)–O(2)	1.229(4)
N(1)–Mo–N(2)	94.55(10)	N(1)–Mo–O(1)	175.91(10)
N(2)–Mo–O(1)	83.75(9)	N(1)–Mo–Cl(3)	93.92(8)
N(2)–Mo–Cl(3)	98.64(7)	O(1)–Mo–Cl(3)	82.69(7)
N(1)–Mo–Cl(1)	97.86(8)	N(2)–Mo–Cl(1)	88.23(7)
O(1)–Mo–Cl(1)	85.82(7)	Cl(3)–Mo–Cl(1)	165.86(3)
N(1)–Mo–Cl(2)	97.65(8)	N(2)–Mo–Cl(2)	166.07(7)
O(1)–Mo–Cl(2)	84.50(6)	Cl(3)–Mo–Cl(2)	87.24(3)
Cl(1)–Mo–Cl(2)	83.47(3)	C(1)–N(1)–Mo	177.8(2)
C(13)–N(2)–Mo	133.0(2)	C(19)–O(1)–Mo	134.7(2)

Table 5 Selected bond lengths (Å) and angles (°) for complex **5**

Mo–O(1)	2.1266(13)	Mo–N(1)	2.221(2)
Mo–N(2)	1.719(2)	Mo–Cl(1)	2.3750(5)
Mo–Cl(2)	2.3972(5)	Mo–Cl(3)	2.4256(5)
N(1)–C(2)	1.508(2)	O(1)–C(1)	1.277(2)
O(2)–C(1)	1.231(2)	N(2)–C(16)	1.449(2)
N(2)–Mo–O(1)	166.20(6)	N(2)–Mo–N(1)	91.67(7)
O(1)–Mo–N(1)	74.54(5)	N(2)–Mo–Cl(1)	103.34(5)
O(1)–Mo–Cl(1)	90.45(4)	N(1)–Mo–Cl(1)	164.98(4)
N(2)–Mo–Cl(2)	94.99(5)	O(1)–Mo–Cl(2)	84.79(4)
N(1)–Mo–Cl(2)	86.86(5)	Cl(1)–Mo–Cl(2)	92.33(2)
N(2)–Mo–Cl(3)	95.41(5)	O(1)–Mo–Cl(3)	83.39(4)
N(1)–Mo–Cl(3)	85.67(5)	Cl(1)–Mo–Cl(3)	92.24(2)
Cl(2)–Mo–Cl(3)	167.36(2)	C(2)–N(1)–Mo	115.82(11)
C(1)–O(1)–Mo	123.15(11)	C(16)–N(2)–Mo	166.93(13)

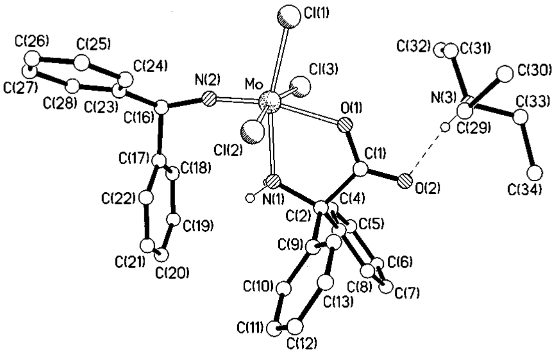


Fig. 5 Molecular structure of complex **5**; details as in Fig. 1

2-Aminoterephthalic acid

Treatment of Na$_2$MoO$_4$ with 2 equivalents of 2-aminoterephthalic acid under analogous conditions affords after work-up red prisms of complex **6** in 32% isolated yield. As expected, the IR spectrum contains strong stretches in the ν(C=O) region together with sharp bands in the ν(N−H) region. A single-crystal structure determination revealed disorder in the ligands, the cation and the dme solvent. Nevertheless, the overall identification of the complex and definition of the co-ordination geometry at molybdenum are clear (Fig. 6, Scheme 1, Table 6).

The co-ordination geometry can thus be described as octahedral with distortion caused by the restricted bite angle of the chelating amidobenzoate ligand. The O(2) atom of this ligand is involved in hydrogen bonding to the cation Et$_3$NH$^+$. The amide proton on N(1) is hydrogen bonded to the O(5) atom of the carboxylate group on the near linear organoimido ligand [Mo−N(2)−C(9) 167.2(3)°]. Further hydrogen bonding links anions in pairs *via* the commonly observed type of centrosymmetric double hydrogen bonding of carboxylic acids, here involving O(3) and O(4), and then into chains by a weaker interaction from O(7)−H to Cl(3) on an adjacent anion.

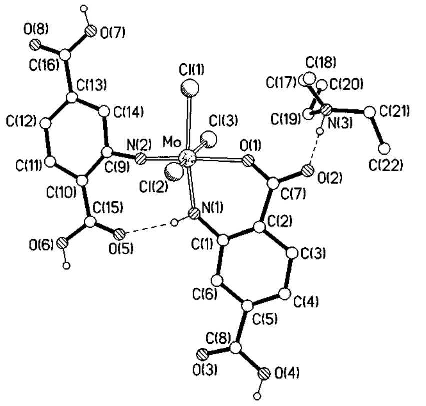
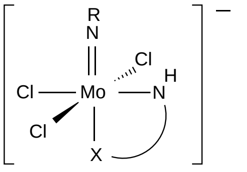


Fig. 6 Molecular structure of complex **6**; details as in Fig. 1



I

In conclusion, molybdenum imido complexes bearing highly functionalised substituents can be prepared conveniently in moderate yields *via* the 'molybdate route'. Instead of affording bis(imido)molybdenum products, our results show that anionic monoimido complexes are favoured in most cases, with intramolecular and/or interionic hydrogen-bonding interactions. The X-ray crystallographic studies reveal a common structural motif (**I**) for the anions of these salts. It is noted that a closely related motif has been seen in hydrazido(2−) products arising from the molybdate reaction.[6]

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Departments of Chemistry at Durham, Imperial College and Medac Ltd. The NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 (^{1}H) and 75.0 MHz (^{13}C) and, where stated, a Bruker DRX 300 machine (^{1}H, 300 MHz); chemical shifts are referenced to the residual protio impurity of the deuteriated solvent. The ESR spectra were recorded on a Varian E-12 (X-band) spectrometer. Infrared spectra (Nujol mulls, KBr windows) were obtained on Perkin-Elmer 577 and 457 grating spectrophotometers. All chemicals were obtained commercially and used as received unless stated otherwise.

Preparations

[NEt$_3$H][MoCl$_3${2-(HN)C$_6$H$_4$CO$_2$}{2-Me$_3$SiO$_2$CC$_6$H$_4$N}] 1. Triethylamine (13.6 cm^3, 97.6 mmol) and SiMe$_3$Cl (24.7 cm^3, 194.6 mmol) were added to Na$_2$MoO$_4$ (5.0g, 24.3 mmol) in dme (150 cm^3). Anthranilic acid (6.66 g, 48.6 mmol) in dme (*ca.* 40 cm^3) was added and the reaction mixture refluxed for 12 h affording a purple solution and a white precipitate. The solution was filtered from the solid which was then washed with dme (2 × 50 cm^3). The solvent was then removed from the combined washings under reduced pressure. Recrystallisation from hot MeCN gave complex **1** as purple prisms. Yield 4.2 g, 27% (Found: C, 43.5; H, 5.5; N, 6.6. Calc. for C$_{23}$H$_{34}$Cl$_3$MoN$_3$O$_4$Si: C, 42.7; H, 5.3; N, 6.5%). IR: 3185w, 1676w, 1639w, 1587w, 1557w, 1309s, 1279s, 1255s, 1196w, 1150w, 1094w, 1033w, 981w, 942w, 908w, 838m, 760s, 686w, 662w, 643w and 609w cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 300 MHz, 298 K): δ 15.61 (br s, 1 H, NH), 9.86 (br s, 1 H, Et$_3$N*H*), 8.32–6.61 (9 × m, 8 H, aryl), 3.14 (m, 6 H, CH$_3$C*H*$_2$N), 1.26 (m, 9 H, C*H*$_3$CH$_2$N) and 0.05 (s, 9 H. Me$_3$Si).

Table 6 Selected bond lengths (Å) and angles (°) for complex **6**·dme

Mo–N(1)	1.925(4)	Mo–O(1)	2.093(3)
Mo–N(2)	1.720(3)	Mo–Cl(1)	2.4121(13)
Mo–Cl(2)	2.3922(14)	Mo–Cl(3)	2.4406(13)
N(1)–C(1)	1.380(5)	C(7)–O(1)	1.220(10)
C(7)–O(2)	1.250(10)	C(8)–O(3)	1.223(11)
C(8)–O(4)	1.292(10)	N(2)–C(9)	1.384(5)
C(15)–O(5)	1.202(5)	C(15)–O(6)	1.319(5)
C(16)–O(7)	1.292(13)	C(16)–O(8)	1.256(13)
N(2)–Mo–N(1)	93.81(16)	N(2)–Mo–O(1)	171.06(17)
N(1)–Mo–O(1)	82.19(16)	N(2)–Mo–Cl(2)	98.62(13)
N(1)–Mo–Cl(2)	87.95(12)	O(1)–Mo–Cl(2)	89.26(11)
N(2)–Mo–Cl(1)	96.93(12)	N(1)–Mo–Cl(1)	168.46(12)
O(1)–Mo–Cl(1)	87.74(12)	Cl(2)–Mo–Cl(1)	86.29(5)
N(2)–Mo–Cl(3)	89.56(12)	N(1)–Mo–Cl(3)	96.82(12)
O(1)–Mo–Cl(3)	83.02(11)	Cl(2)–Mo–Cl(3)	170.26(4)
Cl(1)–Mo–Cl(3)	87.49(5)	C(1)–N(1)–Mo	133.2(4)
C(7)–O(1)–Mo	139.1(6)	C(9)–N(2)–Mo	167.2(3)

[NEt$_3$H]$_2$[MoCl$_3${2-NC$_6$H$_4$SO$_3$}{2-(HN)C$_6$H$_4$SO$_3$}] 2. As above using NEt$_3$ (8.1 cm^3, 58.1 mmol), SiMe$_3$Cl (14.9 cm^3, 117.4 mmol), Na$_2$MoO$_4$ (3.0 g, 14.6 mmol) and 2-(H$_2$N)-C$_6$H$_4$SO$_3$H (5.1 g, 29.4 mmol) in dme (100 cm^3). Recrystallisation from MeCN gave large red needles of complex **2** (yield 3.9 g, 36%) (Found: C, 39.9; H, 6.1; N, 7.6. Calc. for C$_{24}$H$_{41}$-Cl$_3$MoN$_4$O$_6$S$_2$: C, 38.5; H, 5.5; N, 7.5%). IR: 3337 (br), 3084w, 2625w, 2531w, 1571w, 1270s, 1259s, 1170s, 1158s, 1140s, 1082s, 1036s, 1019s, 1011s, 989s, 967m, 917m, 873w, 851w, 837w, 808w, 776s, 732m, 722s, 679w, 657m, 617s, 595m, 572m, 548m, 538m, 511w, 477w and 463w cm^{-1}. NMR (CDCl$_3$, 298 K): ^{1}H (300 MHz), δ 16.49 (s, 1 H, NH), 10.63 (br s, 2 H, Et$_3$N*H*), 8.02–7.14 (6 × m, 8 H, aryl), 3.07 (m, 12 H, CH$_3$C*H*$_2$N) and 1.29 (m, 18 H, C*H*$_3$CH$_2$N); ^{13}C (75.0 MHz), δ 149.6, 132.16, 131.73, 130.60, 130.39, 128.15, 121.79, 46.40 and 8.89.

[MoCl$_2$(2-NCC$_6$H$_4$N)$_2$(dme)] 3. As above using NEt$_3$ (8.1 cm^3, 58.1 mmol), SiMe$_3$Cl (14.9 cm^3, 117.4 mmol), Na$_2$MoO$_4$ (3.0 g, 14.6 mmol) and 2-cyanoaniline (3.45 g, 29.2 mmol) in MeCN (100 cm^3). Extraction into hot dme (*ca.* 80 cm^3) afforded red needles, which were washed twice with cold diethyl ether (*ca.* 2 × 30 cm^3) and dried *in vacuo*. Yield 4.2 g, 59% (Found: C, 44.8; H, 6.0; N, 10.9. Calc. for C$_{18}$H$_{18}$Cl$_2$MoN$_4$O$_2$: C, 44.2; H, 6.5; N, 11.4%). IR: 2361w, 2342w, 2227w, 1935w, 1732w, 1715w, 1624w, 1606w, 1563m, 1306m, 1262s, 1183w, 1156m, 1101s, 1085s, 1037s, 975m, 882w, 864m, 801s, 775m, 761m, 723m, 660w, 616w and 591w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 298 K): δ 8.23–6.73 (several m, 8 H, aryl) and 4.05 (br s, 10 H, dme).

[NEt$_3$H][MoCl$_3${2-(HN)C$_6$H$_4$CO$_2$}(NC$_6$H$_3$Pr$^i_2$-2,6)] 4. As above using NEt$_3$ (8.1 cm^3, 58.1 mmol), SiMe$_3$Cl (14.9 cm^3, 117.4 mmol), anthranilic acid (2.0 g, 14.6 mmol), 2,6-Pr$^i_2$C$_6$H$_3$NH$_2$ (2.77 cm^3, 14.7 mmol) and Na$_2$MoO$_4$ (3.0 g, 14.6 mmol) in dme (100 cm^3). Extraction into warm MeCN (*ca.* 80 cm^3) afforded red-purple prisms. Yield 4.0 g. Further crops can be obtained from the mother-liquor. Overall yield 6.1 g, 61% (Found: C, 49.4; H, 6.3; N, 8.4. Calc. for C$_{25}$H$_{38}$Cl$_3$MoN$_3$O$_2$·MeCN: C, 49.4; H, 6.3, N, 8.5%). IR: 3495w, 3466w, 3438w, 3372w, 2335w, 1963w, 1756w, 1599s, 1561s, 1349s, 1303m, 1260m, 1228m, 1152m, 1104w, 1058w, 1029w, 917w, 886w, 835w, 805w, 764w, 724w, 690w, 657w, 504w, 464w and 429w cm^{-1}. NMR (CDCl$_3$,

Table 7 Crystallographic data for compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**·dme
Formula	$[C_6H_{16}N][C_{17}H_{18}Cl_3MoN_2O_4Si]$	$[C_6H_{16}N]_2[C_{12}H_9Cl_3MoN_2O_6S_2]$	$C_{18}H_{18}Cl_2MoN_4O_2$	$[C_6H_{16}N][C_{19}H_{22}Cl_3MoN_2O_2]$	$[C_6H_{16}N][C_{27}H_{23}Cl_3MoN_2O_2]$	$[C_6H_{16}N][C_{16}H_{10}Cl_3MoN_2O_8]\cdot C_4H_{10}O_2$
M	646.9	748.0	489.2	614.9	712.0	752.9
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$Pbca$	$P\bar{1}$	$P2_1/n$
a/Å	10.1216(11)	9.1981(8)	24.565(2)	13.0324(10)	10.9433(8)	9.2009(5)
b/Å	10.9746(12)	25.526(2)	8.1609(6)	19.0035(15)	11.4974(8)	33.4055(18)
c/Å	15.302(2)	13.9711(12)	22.507(2)	24.128(2)	14.4936(11)	10.8259(6)
α/°	69.015(2)				92.152(2)	
β/°	84.755(2)	92.036(2)	116.666(2)		104.879(2)	100.771(2)
γ/°	67.205(2)				107.558(2)	
U/Å^3	1460.9(3)	3278.2(5)	4032.0(5)	5975.5(8)	1667.2(2)	3268.8(3)
Z	2	4	8	8	2	4
D_c/g cm^{-3}	1.471	1.516	1.612	1.367	1.418	1.530
μ/mm^{-11}	0.80	0.81	0.94	0.73	0.67	0.70
F(000)	664	1544	1968	2544	734	1544
Crystal size/mm	0.35 × 0.18 × 0.08	0.20 × 0.19 × 0.08	0.67 × 0.23 × 0.12	0.40 × 0.34 × 0.26	0.62 × 0.57 × 0.54	0.35 × 0.25 × 0.14
θ_{max}/°	25.6	26.0	26.4	28.6	28.3	25.0
Maximum indices *hkl*	12, 13, 18	12, 32, 18	30, 9, 28	17, 24, 32	13, 14, 19	12. 44. 14
Reflections measured	12 720	18 636	21 008	35 187	10 261	16 922
Unique reflections	4809	6436	7949	7140	7140	5721
R_{int}	0.0528	0.0488	0.0640	0.0561	0.0261	0.0282
Transmission	0.779–0.913	0.776–0.937	0.552–0.962	0.775–0.824	0.658–0.693	0.787–0.901
Extinction coefficient x	0.0026(4)	0.000 80(15)	0.0017(2)	0.000 66(5)	0.0034(5)	0.0017(3)
Weighting parameters a, b	0.0070, 4.2304	0.0214, 8.0491	0.0576, 12.1678	0.0135, 9.0399	0.0385, 1.3171	0.0564, 8.2943
No. refined parameters	329	414	492	315	389	618
$wR2$ (all data)	0.1022	0.1049	0.1412	0.0873	0.0838	0.1347
$R1$ ('observed' data)	0.0504 (4269)	0.0474 (5161)	0.0530 (6970)	0.0501 (5661)	0.0314 (6935)	0.0515 (4644)
Goodness of fit	1.167	1.208	1.192	1.223	1.142	1.084
Maximum, minimum electron density/e Å^{-3}	0.47, −0.68	1.27, −0.47	1.37. −1.37	0.42, −0.53	0.62, −1.23	0.84, −0.98

298 K): ^{1}H (400 MHz), δ 12.52 (s, 1 H, NH), 11.04 (br s, 1 H, Et_3NH), 8.27 (d, 1 H, J_{HH} = 7.6, aryl), 7.44–7.04 (several m, 4 H, aryl), 6.63 (d, 1 H, J_{HH} = 8.4, aryl), 4.55 (spt, 2 H, J_{HH} = 6.8, $CHCMe_2$), 3.33 (m, 6 H, CH_3CH_2N), 1.94 (s, 3 H, CH_3CN), 1.32 [d, 12 H, J_{HH} = 6.8 Hz, $(CH_3)_2CH$] and 1.31 (m, 9 H, CH_3CH_2N, J_{HH} obscured); ^{13}C-{^{1}H}, δ 169.47, 153.56, 151.92, 149.48, 132.99, 131.94, 131.29, 130.97, 126.82, 123.61, 121.16, 45.93, 28.23, 25.47 and 8.82.

$[NEt_3H][MoCl_3(NCHPh_2)(H_2NCPh_2CO_2)]$ 5. As above using NEt_3 (2.7 cm^3, 19.4 mmol), $SiMe_3Cl$ (5.0 cm^3, 39.4 mmol), Na_2MoO_4 (1.0 g, 4.9 mmol) and 2,2-diphenylglycine (2.3 g, 10.1 mmol) in dme (50 cm^3). Extraction into hot MeCN (*ca.* 40 cm^3) afforded turquoise prisms of complex **5**. Yield 1.24 g, 62% (Found: C, 55.5; H, 6.0; N, 6.3. Calc. for $C_{33}H_{38}Cl_3MoN_3O_2$: C, 55.7; H, 5.4; N, 5.9%). IR: 3329w, 3273w, 2670w, 2609w, 2498w, 1631s, 1558m, 1264m, 1227m, 1168w, 1135m, 1060w, 1029w, 1014m, 920w, 822m, 779w, 735w, 679w and 632w cm^{-1}. EPR (solid, 298 K): g_{iso} 1.953.

$[NEt_3H][MoCl_3\{2\text{-}HNC_6H_3CO_2(CO_2H)\text{-}1,4\}\{2\text{-}NC_6H_3(CO_2H)_2\text{-}1,4\}]$ 6. As above using NEt_3 (8.1 cm^3, 58.3 mmol), $SiMe_3Cl$ (14.8 cm^3, 116.5 mmol), Na_2MoO_4 (3.0 g, 14.6 mmol) and 2-aminoterephthalic acid (5.28 g, 29.2 mmol). The crystals were dried *in vacuo* overnight to remove dme solvent of crystallisation. Yield 3.1 g, 32% (Found: C, 39.9; H, 4.4; N, 5.3. Calc. for $C_{22}H_{28}Cl_3MoN_3O_8$: C, 39.8; H, 4.3; N, 6.3%). IR: 3383m, 1681s, 1622s, 1591s, 1553m, 1495m, 1300s, 1261s, 1230s, 1156s, 1093s, 1053s, 1020s, 944m, 908m, 839w, 801s, 753s, 723s, 684w, 665w, 647w, 567w, 558w, 519w, 485w, 647w and 427w cm^{-1}.

X-Ray crystallography

Crystal data and other information on the structure determinations are given in Table 7. All measurements were made at 160 K on a Siemens SMART CCD diffractometer with Mo-Kα radiation (λ = 0.71 073 Å).[7] Cell parameters were refined from observed setting angles of all strong reflections in each complete data set, which consisted of more than a hemisphere of data measured from several series of narrow-frame exposures (0.3° in ω).[7] Analysis of redundant and symmetry-equivalent reflections indicated no significant intensity decay, and formed the basis for semiempirical absorption corrections.[8]

The structures were solved variously by heavy-atom and direct methods, and were refined on F^2 values for all reflections,[8] with weighting $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. An isotropic extinction coefficient x was refined, whereby $F'_c = F_c/(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{\frac{1}{4}}$. Disorder was resolved for one cation of complex **2**, and for the organic ligands, cation and dme solvent of **6**·dme, and was successfully refined with the aid of geometrical and displacement parameter restraints; for the dme molecule no sensible geometry could be found, and the disorder model consisted of eleven partially occupied sites, all treated as carbon. Anisotropic displacement parameters were refined for non-hydrogen atoms. Hydrogen atoms were made to ride on the atoms to which they were attached, except for free refinement of the N−H groups in the ligands, which (together with most of the other H atoms) were revealed in difference electron-density maps. A pseudo-orthorhombic A-centred unit cell can be generated for the structure of **3**, by the transformation (0 1 0 / 0 0 − 1 / − 2 0 − 1); this gives a value of over 0.5 for R_{int}, however, and one of the cell angles is 89.4°, so the true symmetry is monoclinic as reported. The two independent molecules are related by an approximate non-crystallographic inversion centre with coordinates close to (0.25, 0.51, 0.33). Residual indices are defined as $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all data, conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $F_o^2 > 2\sigma(F_o^2)$; the goodness of fit was calculated on all F^2 values.

Atomic coordinates, displacement parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/559.

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