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Compounds in which the Mo_2^{4+} unit is embraced by one, two or three formamidinate ligands together with acetonitrile ligands

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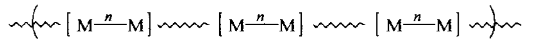
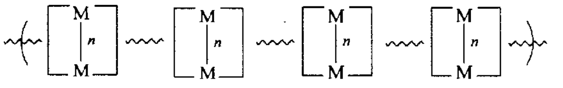
The cationic complexes $[Mo_2(DPhF)(MeCN)_6]^{3+}[BF_4^-]_3\cdot MeCN$ **1a** [throughout this paper the formamidinate anions, $RNC(H)NR^-$, will be abbreviated as DRF^-, with specific aryl groups represented by Ph for phenyl, and Ani for *p*-anisyl], $[Mo_2(DAniF)(MeCN)_6]^{3+}[BF_4^-]_3\cdot 1.59MeCN$ **1b**, *cis*-$[Mo_2(DPhF)_2(MeCN)_4]^{2+}[BF_4^-]_2\cdot MeCN$ **2a**, *cis*-$[Mo_2(DAniF)_2(MeCN)_4]^{2+}[BF_4^-]_2\cdot 2MeCN$ **2b**, and $[Mo_2(DPhF)_3(MeCN)_2]^+[BF_4^-]$ **3**, have been prepared from the reactions between $Mo_2(DArF)_4$ and $HBF_4\cdot Et_2O$ or $(Me_3O)BF_4$ in an appropriate stoichiometry in acetonitrile or CH_2Cl_2–MeCN mixtures. A better procedure for the preparation of **3** involves the reaction between **2a** and $Li^+(DPhF^-)$ in acetonitrile. Compound **2a** undergoes a reaction in pyridine to give the compound *trans*-$[Mo_2(DPhF)_2(py)_4]^{2+}[BF_4^-]_2$ **4**. The new compounds **1a**, **1b**, **2a**, **2b** and **4** have been structurally characterized and shown to contain Mo–Mo quadruple bonds.

Introduction

In previous work[1] attempts have been made to link M–M multiply bonded complexes, bridged by carboxylates, together to form parallel or perpendicular polymers of the type shown below in **I** and **II**, respectively.



I



II

Unfortunately for such oligomers of molybdenum and tungsten supported by carboxylate ligands, ligand scrambling occurred and rendered the polymers and smaller oligomers kinetically labile. Indeed, even a linked dimer of "dimers" was susceptible to disproportionation of the type shown in eqn. (1).

$$[M_2(O_2CR)_3]_2(\text{bridge}) \rightleftharpoons M_2(O_2CR)_4 + 1/n[M_2(O_2CR)_2(\text{bridge})]_n \quad (1)$$

Reactions of type (1) arise because the M_2^{4+} centers, where M = Mo and W, are kinetically labile to substitution reactions. Carboxylate scrambling can be catalyzed by adventitious carboxylate anions or acid present in solution.[2] In order to minimize such facile ligand scrambling we reasoned that the use of ligands lacking the active lone pairs of carboxylates might lead to more kinetically persistent linked di- and poly-nuclear species. As the first part of the continuing project in developing such systems, we report here the synthesis and characterization of cationic formamidinate bridged dimolybdenum complexes which, unlike their Mo_2–carboxylate counterparts, are much less labile to ligand scrambling. A few examples of how they might be linked have been reported,[3] but many more will be described in the near future.[4]

Results and discussion

Synthesis

This investigation was carried out independently by the groups at Indiana University and at Texas A&M University; one worked with the ligand DPhF $[PhNC(H)NPh^-]$, while the other worked with the anisyl (Ani) analogue, DAniF $[AniNC(H)NAni^-]$. Though the synthetic procedures employed by both groups are fairly similar, there are important differences which make some comparison worthwhile. The general synthetic strategy for the formation of phenyl derivatives of $Mo_2(DPhF)_{4-n}{}^{n+}$ cationic complexes is shown in eqn. (2).

$$Mo_2(DPhF)_4 + 2nHBF_4\cdot Et_2O \xrightarrow[\text{MeCN}]{25\,°C} [Mo_2(DPhF)_{4-n}(MeCN)_{2n}]^{n+}[BF_4^-]_n + n[H_2DPhF]^+[BF_4^-]_n \quad (2)$$

Reaction (2) is complicated by the fact that $Mo_2(DPhF)_4$ is very sparingly soluble in MeCN as a solvent. Thus, the reaction proceeds by the addition of $HBF_4\cdot Et_2O$ to a slurry of $Mo_2(DPhF)_4$. The resultant cationic Mo_2 species are more soluble and thus go into solution. As a consequence the addition of $HBF_4\cdot Et_2O$ must proceed slowly if any control of product is desired beyond formation of the $Mo_2(MeCN)_8{}^{4+}$ and $Mo_2(DPhF)(MeCN)_6{}^{3+}$ salts. To this end it is desirable to dilute the $HBF_4\cdot Et_2O$ in MeCN solution and to add the acid slowly.

All the species have somewhat different solubilities and colors. The $Mo_2(MeCN)_8{}^{4+}$ cation is blue; $Mo_2(DPhF)(MeCN)_6{}^{3+}$ **1a** is purple; $Mo_2(DPhF)_2(MeCN)_4{}^{2+}$, **2a** is red and $Mo_2(DPhF)_3(MeCN)_2{}^+$ **3** is pumpkin orange while $Mo_2(DPhF)_4$ is yellow. The most difficult compound in the series to obtain is $[Mo_2(DPhF)_3(MeCN)_2]^+[BF_4^-]$ **3**, which in our hands was best prepared by the reaction shown in eqn. (3).

$$[Mo_2(DPhF)_2(MeCN)_4]^{2+}[BF_4^-]_2 + LiDPhF \xrightarrow[\text{MeCN}]{25\,°C} [Mo_2(DPhF)_3(MeCN)_2]^+[BF_4^-] + Li^+BF_4^- \quad (3)$$

Table 1 Selected bond distances (Å) for $[Mo_2(DPhF)(MeCN)_6]^{3+}$-$[BF_4^-]_3$·MeCN **1a**

Mo(1)–Mo(2)	2.149(1)	Mo(39)–Mo(40)	2.151(1)
Mo(1)–N(9)	2.086(8)	Mo(39)–N(47)	2.098(8)
Mo(1)–N(18)	2.58(1)	Mo(39)–N(56)	2.567(9)
Mo(1)–N(21)	2.150(9)	Mo(39)–N(59)	2.129(9)
Mo(1)–N(24)	2.19(1)	Mo(39)–N(62)	2.165(9)
Mo(1)–N(27)	2.124(9)	Mo(39)–N(65)	2.15(1)
Mo(2)–N(11)	2.078(8)	Mo(40)–N(49)	2.076(8)
Mo(2)–N(30)	2.14(1)	Mo(40)–N(68)	2.139(9)
Mo(2)–N(33)	2.168(9)	Mo(40)–N(71)	2.173(9)
Mo(2)–N(36)	2.11(1)	Mo(40)–N(74)	2.13(1)

Dissolving $[Mo_2(DPhF)_2(MeCN)_4]^{2+}[BF_4^-]_2$ in pyridine leads to a facile replacement of the MeCN ligands by pyridine and a slow isomerization to give *trans*-$[Mo_2(DPhF)_2(py)_4]^{2+}[BF_4^-]_2$ **4**.

The anisyl analogues were prepared by slightly modified procedures which offered more control over the reaction, especially for the preparation of **2b**.

Compound **1b** was prepared in a 1:4 mixture of acetonitrile and dichloromethane.

$$Mo_2(DAniF)_4 + HBF_4{\cdot}Et_2O(\text{excess}) \xrightarrow[\text{MeCN–CH}_2\text{Cl}_2]{25\,^\circ\text{C}} [Mo_2(DAniF)(MeCN)_6][BF_4^-]_3 + 3\,[H_2DAniF][BF_4] \quad (4)$$

Under these conditions it is not necessary to control the rate of addition of $HBF_4{\cdot}Et_2O$. Furthermore, $Mo_2(DAniF)_4$ and $[H_2DAniF][BF_4]$ are soluble in this mixture, and therefore the only species that precipitates is the purplish **1b**.

For the preparation of **2b** we found that the use of wet $(Me_3O)BF_4$ is more advantageous than neat $HBF_4{\cdot}Et_2O$.

$$Mo_2(DAniF)_4 + (Me_3O)BF_4(\text{excess}) + 4H_2O \xrightarrow[\text{MeCN}]{25\,^\circ\text{C}} [Mo_2(DAniF)_2(MeCN)_4][BF_4^-]_2 + 2\,[H_2DAniF][BF_4] + Me_2O + 4\,MeOH \quad (5)$$

An acetonitrile slurry of $(Me_3O)BF_4$ and $Mo_2(DAniF)_4$ does not react but addition of a small amount of deoxygenated water slowly dissolves all of the $Mo_2(DAniF)_4$ producing a clear red solution. After removal of the solvent, the solid is washed with Et_2O, then recrystallized from a mixture of CH_2Cl_2–MeCN which is layered with Et_2O to produce an essentially quantitative yield of **2b**.

Structural characterizations

$[Mo_2(DPhF)(MeCN)_6]^{3+}[BF_4^-]_3$·MeCN 1a. In the unit cell of space group $P2_1/n$ there are two $[Mo_2(DPhF)(MeCN)_6]^{3+}$ cations and six BF_4^- anions. The Mo–Mo distances, 2.15(1) Å, are essentially identical for both molecules and the gross structural features are very similar. The Mo–N (formamidinate) distances 2.08(1) Å (average) are shorter by 0.05 to 0.10 Å than the Mo–N distances to the acetonitrile ligands. Each Mo atom is coordinated to four N atoms that lie roughly in a plane and the central Mo_2N_8 skeleton is virtually eclipsed as expected for Mo–Mo quadruply bonded complexes. In addition, there is a weak, 2.58 Å, interaction between Mo(1) and an axial MeCN. Selected bond distances are given in Table 1.

$[Mo_2(DAniF)(MeCN)_6]^{3+}[BF_4^-]_3$·1.59MeCN 1b. Compound **1b** crystallizes in space group $P\bar{1}$ with the three BF_4^- groups and the weakly-interacting axial MeCN groups all disordered to some extent. One axial position is fully occupied although the MeCN group has two orientations in the approximate ratio of 53:47. The MeCN group at the other axial position has a refined occupancy of 59%. Two of the BF_4^- sites were modeled as two interpenetrating tetrahedra. The third anion did not behave as well and the ensemble of electron density was simply modeled as a group of 8 F atoms of variable occupancy, with the total occupancy constrained to equal 4. Again, the Mo_2N_8 core is essentially eclipsed (torsion angles all less than 2°) as expected. The axial interactions are very weak, with Mo–N distances of 2.70 and 2.82 Å.

A view of the molecule is given in Fig. 1. Selected bond distances are given in Table 2.

Table 2 Selected bond distances (Å) for $[Mo_2(DAniF)(MeCN)_6]^{3+}$-$[BF_4^-]_3$·1.59MeCN **1b**

Mo(1)–Mo(2)	2.152(1)	Mo(2)–N(2)	2.09(1)
Mo(1)–N(1)	2.09(1)	Mo(2)–N(4)	2.15(1)
Mo(1)–N(3)	2.14(1)	Mo(2)–N(6)	2.14(1)
Mo(1)–N(5)	2.17(1)	Mo(2)–N(8)	2.13(1)
Mo(1)–N(7)	2.13(1)		

Table 3 Selected bond distances (Å) for *cis*-$[Mo_2(DPhF)_2$-$(MeCN)_4]^{2+}[BF_4^-]_2$·MeCN **2a**

Mo(1)–Mo(2)	2.1457(7)	Mo(2)–N(5)	2.118(3)
Mo(1)–N(3)	2.086(3)	Mo(2)–N(20)	2.105(3)
Mo(1)–N(18)	2.100(3)	Mo(2)–N(39)	2.180(3)
Mo(1)–N(33)	2.181(3)	Mo(2)–N(42)	2.185(3)
Mo(1)–N(36)	2.183(3)	Mo(2)–N(45)	2.595(3)

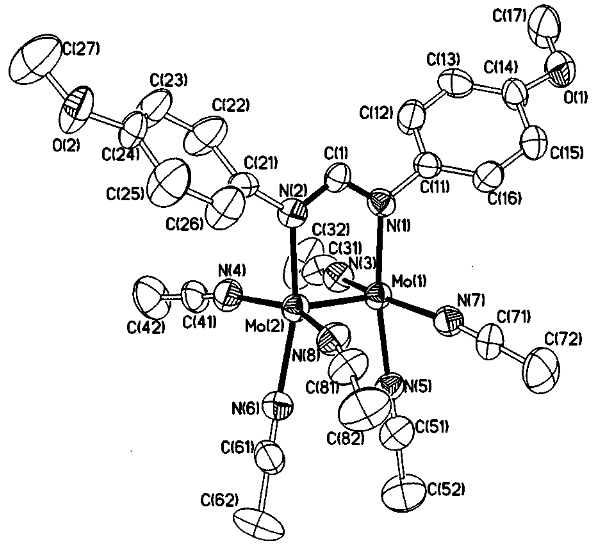


Fig. 1 A view of the $[Mo_2(DAniF)(MeCN)_6]^{3+}$ cation in **1b**, with ellipsoids drawn at the 40% probability level.

***cis*-$[Mo_2(DPhF)_2(MeCN)_4]^{2+}[BF_4^-]_2$·MeCN 2a.** Compound **2a** crystallizes in the space group $P\bar{1}$ with two formula units in the unit cell. One MeCN molecule is weakly ligated in an axial position to one of the Mo atoms, namely Mo(2) *via* a long, 2.595(3) Å, interaction. Selected bond distances are given in Table 3. The two μ-formamidinate ligands are mutually *cis* and the shortest Mo–N distances involve formamidinate nitrogen atoms that are bound to Mo(1) which has only two attendant MeCN ligands. The Mo–Mo distance of 2.1457(7) Å is comparable to that in **1** and only somewhat longer than that in $Mo_2(DPhF)_4$, 2.0944(8) Å.[5]

***cis*-$[Mo_2(DAniF)_2(MeCN)_4]^{2+}[BF_4^-]_2$·2MeCN 2b.** Compound **2b** also crystallizes in the space group $P\bar{1}$; the structure is very similar to that of its phenyl analogue. The Mo–Mo distance of 2.1439(6) Å is equivalent to that of **2a**. A view of the dication, shown in Fig. 2, reveals that a coordinated acetonitrile molecule is located at a distance of 2.590(4) Å from Mo(1). All other chemically equivalent dimensions are comparable for **2a** and **2b**. Selected bond distances are given in Table 4.

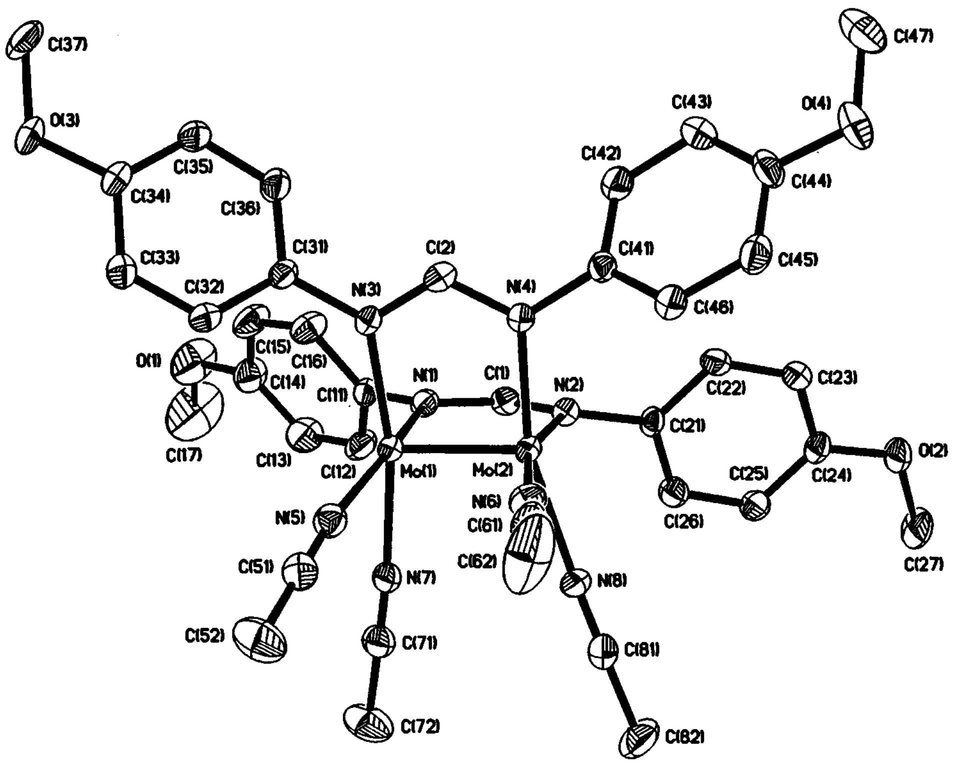


Fig. 2 A drawing of the cation *cis*-$[Mo_2(DAniF)_2(MeCN)_4]^{2+}$ in **2b**, with ellipsoids drawn at the 40% probability level.

Table 4 Selected bond distances (Å) for *cis*-$[Mo_2(DAniF)_2(MeCN)_4]^{2+}[BF_4^-]_2\cdot 2MeCN$ **2b**

Mo(1)–Mo(2)	2.1439(6)	Mo(2)–N(2)	2.085(3)
Mo(1)–N(1)	2.115(3)	Mo(2)–N(4)	2.087(3)
Mo(1)–N(3)	2.117(3)	Mo(2)–N(6)	2.172(3)
Mo(1)–N(7)	2.185(3)	Mo(2)–N(8)	2.180(3)
Mo(1)–N(5)	2.188(3)		

Table 5 Selected bond distances (Å) and angles (°) for *trans*-$[Mo_2(DPhF)_2(py)_4]^{2+}[BF_4^-]_2$ **4**

Mo(1)–Mo(1′)	2.107(2)	Mo(1)–N(17)	2.226(6)
Mo(1)–N(2)	2.151(6)	Mo(1)–N(23)	2.243(5)
Mo(1)–N(4)	2.132(6)		
Mo(1′)–Mo(1)–N(2)	92.6(2)	Mo(1′)–Mo(1)–N(4)	92.3(2)
Mo(1′)–Mo(1)–N(17)	99.6(2)	Mo(1′)–Mo(1)–N(23)	103.8(2)

$[Mo_2(DPhF)_2(py)_4]^{2+}[BF_4^-]_2\cdot 4py$ 4. The asymmetric unit contained one half of the dinuclear unit together with one BF_4^- anion and two molecules of interstitial pyridine. One of the solvent molecules C(40)–C(51) was severely disordered. However, the remainder of the structure was well behaved. A drawing of the centrosymmetric dication is given in Fig. 3 which shows the *trans* arrangement of the formamidinate ligands. Also in Fig. 3 we show a view looking down the Mo–Mo bond which reveals the eclipsed geometry of the ligands and the favorable π–π stacking of the pyridine ligands. Selected bond distances and angles are given in Table 5. Of note is the fact that the Mo–N distances are longer by *ca* 0.1 Å to the pyridine nitrogen atoms than those to the formamidinate nitrogen atoms. Also the Mo–Mo–N angles to the pyridine ligands are larger to accommodate a more favorable π–π stacking.

Electronic spectra

The color of the various anisyl derivatives changes from blue in the unsubstituted $Mo_2(MeCN)_8^{4+}$ cation, to purple for $Mo_2(DAniF)(MeCN)_6^{3+}$ **1b**, to red for $Mo_2(DAniF)_2(MeCN)_4^{2+}$ **2b**, and to yellow for $Mo_2(DAniF)_4$. Their lowest transition energies, which were assigned to δ→δ* transitions, are 597, 570, 516 and 430 nm, respectively. This spectroscopic blue shift supports the idea that by increasing the number of the formamidinate ligands, the Mo–Mo bond strength increases. This correlates with the decrease of their Mo–Mo bond distances, which are 2.180,[6] 2.152, 2.144 and 2.096 Å,[5] respectively.

Reactivity studies of the phenyl substituted formamidinates

In CD_3CN as solvent the cationic complexes **1a** and **2a** exhibit facile CH_3CN for CD_3CN exchange. Similarly, for **4** exchange of coordinated py ligands with py-d_5 is rapid. However, our key observations involve the lack of exchange of the formamidinate ligands. Thus, compound **2a** and $Mo_2(DPhF)_4$ failed to yield the compound $[Mo_2(DPhF)_3(MeCN)_2]^+[BF_4^-]$ as judged by NMR spectroscopy in acetonitrile solvent. In part, this could have been attributed to the insolubility of $Mo_2(DPhF)_4$. However, a reaction between compound **2a** and Li(DPhF) in MeCN did yield **3** in conjunction with some formation of $Mo_2(DPhF)_4$ (which could be removed by filtration). Because the solubilities of complex **2a** and complex **3** are very similar, the optimum preparation of **3** involves the reaction between **2a** and Li(DPhF) (1.5 equivalents) in MeCN which results in 90% of **3** and 10% of **2a** after filtration to remove $Mo_2(DPhF)_4$.

We also attempted to study the comproportionation of the dicationic complex **2a** with $[Mo_2(MeCN)_{10}]^{4+}[BF_4^-]_4$[7] in CD_3CN. Here both species are fully dissolved. However, we observed no ligand exchange leading to the formation of the tricationic complex **1** as judged by the ^1H NMR spectroscopy. Thus, in contrast to carboxylate ligands, we find the formamidinate ligands to be relatively inert to ligand scrambling.

The reaction between compound **3** and the oxalate dianion was studied as shown in eqn. (6).

$$2[Mo_2(DPhF)_3(MeCN)_2]^+[BF_4^-] + [Bu^n_4N^+]_2C_2O_4 \xrightarrow[\text{MeCN}]{25\,^\circ C} [Mo_2(DPhF)_3]_2(\mu\text{-}O_2CCO_2) + 2[Bu^n_4N^+][BF_4^-] \quad (6)$$

The product of the reaction was a red-orange powder essentially insoluble in CD_3CN, CD_2Cl_2 and py-d_5. Given the recent

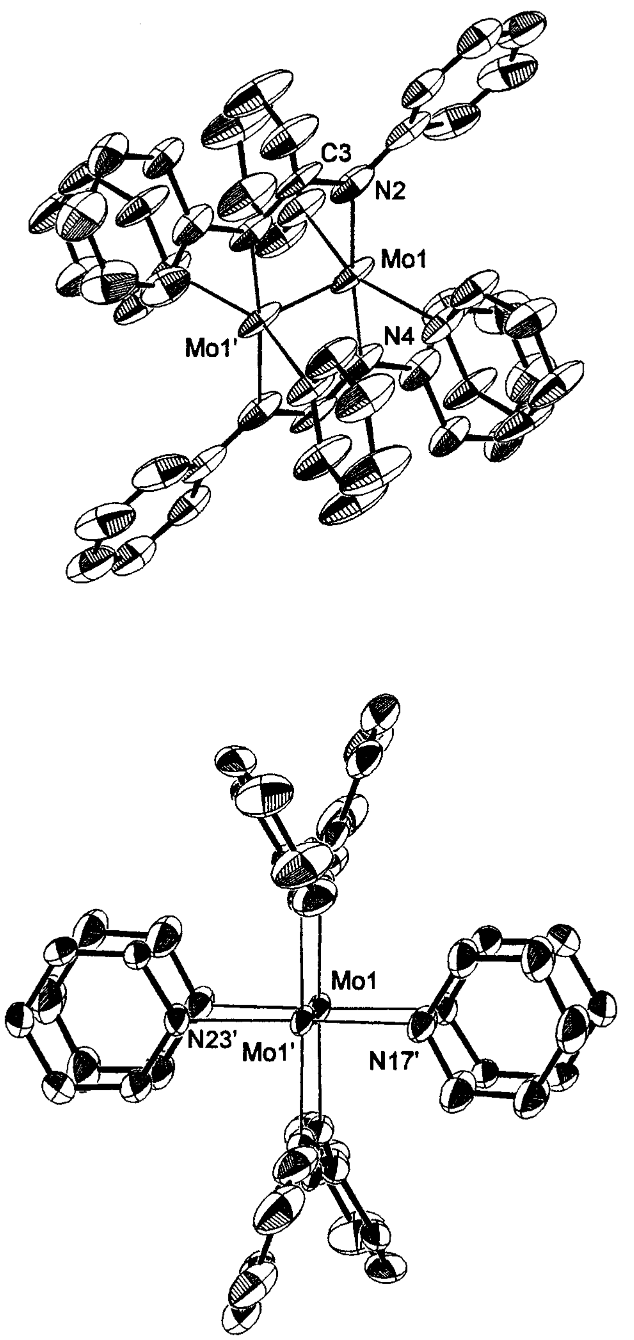


Fig. 3 An ORTEP[10] drawing of $[Mo_2(DPhF)_2(py)_4][BF_4]_2$ **4**, front-on view (top) and looking down the metal–metal bond axis (bottom), with the hydrogen atoms and the BF_4 counter anions omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

report by some of us,[3] we presume that reaction 6 provides an alternate synthesis of the μ-oxalate type complex.

Concluding remarks

In this work we have prepared dimolybdenum cationic complexes supported by one, two and three formamidinate ligands. These have been shown to be notably less labile to ligand scrambling than their related carboxylate counterparts. The success in the preparation of the μ-oxalate linked dimer of "dimers" in reaction (6) suggests that formamidinate ligands may lead to kinetically more persistent quartets (dimers of "dimers") and higher oligomers.

Experimental

All manipulations were carried out under an inert atmosphere by using standard Schlenk and glove-box techniques. All solvents were dried and degassed by standard methods and distilled prior to use. ^1H NMR spectra were recorded on Varian Gemini-2000 and Varian XL-200E NMR spectrometers and referenced to residual protio impurities in the deuteriated solvent. Infrared spectra were obtained as KBr pellets on Nicolet 510 P FT-IR or Perkin-Elmer 16PC FTIR spectrometers. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA or Canadian Microanalytical Service, Delta, BC. Tetrafluoroboric acid (54 wt.% or 85 wt.% in diethyl ether), *N*,*N*′-diphenylformamidine and *n*-butyllithium (1.6 M in hexanes) were purchased from Aldrich Chemical Company and used as received. $Mo_2(DPhF)_4$ was prepared according to the method described previously for $Mo_2[(p\text{-tol})NCHN(p\text{-tol})]_4$ (*p*-tol = *p*-tolyl);[8] the anisyl analogue $Mo_2(DAniF)_4$ was prepared by following a published procedure.[5] Li(DPhF) was obtained by neutralizing a THF solution of *N*,*N*′-diphenylformamidine with 1 equivalent of *n*-butyllithium at −78 °C. After warming to room temperature, the volatile components were removed under vacuum and the resulting off-white solid was washed with hexane.

Syntheses

$[Mo_2(DPhF)(MeCN)_6][BF_4]_3\cdot MeCN$ 1a. A solution of 0.84 mL (6.4 mmol) of $HBF_4\cdot Et_2O$ in 25 mL of MeCN was added dropwise over a 45 min period to a slurry containing 1.0 g (1.02 mmol) of $Mo_2(DPhF)_4$ in 25 mL of acetonitrile. Over this time, the color of the solution changed from pale yellow to plum. The solution was stirred for an additional 2 h to ensure completion and then filtered to remove unreacted $Mo_2(DPhF)_4$. The reaction mixture was concentrated to 10 mL after which 25 mL of diethyl ether was added resulting in the formation of a purple precipitate. The solid was isolated by filtration through a medium frit and dried under vacuum to yield 0.73 g (76%). Deep red crystals suitable for X-ray analysis were obtained by cooling a concentrated solution of **1**, in MeCN, to −15 °C for several days. ^1H NMR (CD_3CN): δ 9.05 (s, 1H), 7.3 (m, 4H), 7.2 (m, 6H), 1.95 (s, 11H). IR (cm^{-1}): 1599w, 1520m, 1450m, 1322m, 1217m, 1063vs (br), 761s, 699m, 692m, 520w, 461m.

$[Mo_2(DAniF)(MeCN)_6][BF_4]_3\cdot 1.59MeCN$ 1b. To a stirred solution of $Mo_2(DAniF)_4$ (150 mg, 0.124 mmol) in 20 mL of CH_2Cl_2 and 5 mL of MeCN, was added 0.3 mL of $HBF_4\cdot Et_2O$ (85% in Et_2O). The yellow color quickly changed to red then purple. The reaction mixture was stirred at room temperature for 30 min. Diethyl ether (20 mL) was added. Then the solvent was decanted off and the solid residue was extracted into MeCN (3 mL) and then filtered. The crystalline product was obtained by addition of CH_2Cl_2 (30 mL) to the filtrate. Yield, 100 mg (85%). Purple single crystals suitable for X-ray analysis were grown by diffusion of Et_2O into a MeCN solution. ^1H NMR (CD_3CN): δ 8.97 (s, 1H, NCHN), 7.15 (d, 4H, aromatic, $^3J = 9.0$), 6.88 (d, 4H, aromatic, $^3J = 9.0$ Hz), 3.75 (s, 6H, OCH_3). IR (KBr, cm^{-1}): 2374w, 2338w, 2283w, 2050w, 1654w, 1637w, 1608m, 1528m, 1505s, 1461m, 1442m, 1401m, 1298m, 1246s, 1214s, 1175s, 1082s, 1035s, 832m, 805w, 767w, 593w, 533w, 522w, 464w. UV-vis, λ_{max}/nm (ε/M^{-1} cm^{-1}): 570 (3130), 460 (2470), 290 (sh).

$[Mo_2(DPhF)_2(MeCN)_4][BF_4]_2\cdot MeCN$ 2a. To a slurry of $Mo_2(DPhF)_4$ (0.51 g, 0.51 mmol) in 25 mL of MeCN, a solution of $HBF_4\cdot Et_2O$ (0.28 mL, 2.1 mmol dissolved in 25 mL of MeCN) was added dropwise over a period of several hours. The addition of HBF_4 resulted in a color change from pale yellow to deep red. The mixture was then stirred for an additional 2 h, filtered to remove any unreacted $Mo_2(DPhF)_4$, concentrated and cooled to −15 °C. Over a period of 2 days a red precipitate formed and was isolated by filtration through a medium frit and dried under vacuum to yield 0.343 g (72%). Deep red crystals of

Table 6 Summary of crystal data

	1a	**1b**	**2a**	**2b**	**4**
Empirical formula	$C_{27}H_{32}Mo_2B_3N_9F_{12}$	$C_{30.18}H_{37.77}B_3F_{12}Mo_2N_{9.59}O_2$	$C_{36}H_{37}B_2F_8Mo_2N_9$	$C_{42}H_{48}B_2F_8Mo_2N_{10}O_4$	$C_{66}H_{62}B_2F_8Mo_2N_{12}$
M	934.90	1019.20	961.24	1122.40	1388.79
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	23.831(3)	11.017(8)	12.027(3)	12.323(3)	27.753(6)
b/Å	12.218(1)	11.065(8)	17.335(5)	13.155(2)	12.462(2)
c/Å	26.018(3)	18.77(2)	10.341(3)	16.817(4)	18.715(4)
α/°		87.28(3)	91.76(1)	94.04(1)	
β/°	94.13(0)	85.49(3)	109.71(2)	94.78(1)	106.51(1)
γ/°		82.67(5)	80.43(1)	111.90(1)	
U/Å^3	7555.76	2260(4)	2000.52	2505.4(9)	6205.83
Z	8	2	2	2	4
T/K	104	273	103	213	98
D_c/g cm^{-3}	1.644	1.498	1.596	1.488	1.486
Crystal size/mm	0.25 × 0.25 × 0.40	0.10 × 0.20 × 0.30	0.10 × 0.17 × 0.20	0.25 × 0.25 × 0.20	0.15 × 0.15 × 0.30
μ(Mo-Kα)/cm^{-1}	7.377	6.43	7.027	5.800	4.800
2θ range/°	6–45	4.4–45	6–50	4–46	6–45
No. unique data	9840	5562	7101	6490	4080
$R(F)^a$ or $R(F^2$, all data$)^b$	0.0539 [a]	0.114 [b]	0.0360 [a]	0.058 [b]	0.0632 [a]
$R_w(F)^a$ or $R_w(F^2$, all data$)^b$	0.0473 [a]	0.255 [b]	0.0352 [a]	0.134 [b]	0.0575 [a]
Goodness of fit	1.123	1.256	0.955	1.071	1,359

[a] $R(F) = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$, $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [b] $R(F^2) = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{\frac{1}{2}}$.

2 suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile solution. ^{1}H NMR (CD_3CN): δ 8.8 (s, 1H), 7.1 (m, 6H), 6.7 (d, 4H, $J = 8.7$ Hz), 1.95 (s, 9H). IR (cm^{-1}): 2849w, 2775vw, 2363w, 1577s, 1491s, 1233m, 1094s (br), 841w, 776m. (Calc. for $Mo_2C_{34}H_{34}N_8B_2F_8$: C, 44.38; H, 3.73; N, 12.18. Found: C, 44.48; H, 3.88; N, 11.85%).

[Mo$_2$(DAniF)$_2$(MeCN)$_4$][BF$_4$]$_2$·2MeCN 2b. A 100 mL, three-necked, round-bottomed flask was charged with 242 mg (0.20 mmol) of Mo_2(DAniF)$_4$, 178 mg (1.20 mmol) of (Me_3O)BF_4, and 60 mL of MeCN. To the stirred suspension was added a small amount of deoxygenated H_2O (*ca.* 2–3 drops). The resulting mixture was stirred at room temperature for *ca.* 5 h, after which time all of the yellow starting material had reacted to give a clear red solution. After the removal of solvent, the red residue was washed with Et_2O (2 × 10 mL), then extracted with CH_2Cl_2–MeCN (19 : 1, 2 × 5 mL). Diethyl ether (75 mL) was then carefully added to the extract, and the solution was stored for 24 h at room temperature. Large orange-red block-shaped crystals formed; they were collected by filtration and dried for 4 h *in vacuo*. The yield was essentially quantitative. Single crystals suitable for X-ray analysis were grown by diffusion of Et_2O into an MeCN solution. ^{1}H NMR (CD_3CN): δ 8.68 (s, 2H, NCHN), 6.69 (m, 16H, aromatic), 3.69 (s, 12H, OCH_3). IR (KBr, cm^{-1}): 2373w, 2314w, 2283w, 2045w, 1695m, 1610m, 1532s, 1506s, 1464m, 1443m, 1342w, 1291m, 1249s, 1215s, 1178m, 1083s, 1030s, 830m, 766w, 723w, 592w, 526w. UV-vis, λ_{max}/nm, (ε/M^{-1} cm^{-1}): 516 (2320), 410 (3430), 287 (sh). (Calc. for $C_{38}H_{42}B_2F_8Mo_2N_8O_4$: C, 43.87; H, 4.07; N, 10.77. Found: C, 43.23; H, 4.07; N, 10.10%).

[Mo$_2$(DPhF)$_3$(MeCN)$_2$][BF$_4$] 3. A 100 mL Schlenk flask was charged with 0.30 g (0.33 mmol) of **2** and 0.096 g (0.49 mmol) of Li(DPhF). To this mixture was added 35 mL of MeCN. The reaction was stirred at room temperature for 12 h, after which time the solution was filtered to remove the Mo_2(DPhF)$_4$, which formed as a result of **3** undergoing additional reaction with Li(PhNCHPh). Removal of the volatile components under dynamic vacuum yielded a pumpkin colored powder that contained 90% of [Mo_2(DPhF)$_3$(MeCN)$_2$][BF_4] and 10% of [Mo_2(DPhF)$_2$(NCMe)$_4$][BF_4]$_2$ by ^{1}H NMR. ^{1}H NMR (CD_3CN): δ 9.1 (s, 2H), 8.4 (s, 1H), 7.1 (m, 8H), 7.0 (m, 4H), 6.8 (m, 6H), 6.7 (d, 8H), 6.2 (d, 4H), 1.95 (s, 5H). IR (cm^{-1}): 2197vw, 1696m, 1595m, 1534vs, 1489vs, 1319s, 1215s, 1063s (br), 758s, 696m, 517w, 434w.

[Mo$_2$(DPhF)$_2$(py)$_4$][BF$_4$]$_2$ 4. To a flask containing 0.2 g (0.19 mmol) of **2** was added 25 mL of pyridine. The reaction was stirred at room temperature for 1 h. After 15 min the color of the solution changed from red to orange. The reaction mixture was filtered through a fine frit, concentrated and left undisturbed at ambient temperature. Hexagonal crystals of **4** suitable for X-ray analysis were obtained after 1 week. The yield is essentially quantitative. ^{1}H NMR (pyridine-d_5): δ 9.9 (s, 1H), 7.6 (d, 4H), 7.5 (m, 6H), 7.2 (m, 25H), 6.7 (d, 4H). IR (cm^{-1}): 2900w, 1600s, 1520s, 1310s, 1094 vs (br), 841w, 776m (Calc. for $Mo_2C_{66}H_{62}N_{12}B_2F_8$: C, 57.08; H, 4.50; N, 12.10. Found: C, 57.10; H, 4.58; N, 12.11%).

Crystallographic study

General operating procedures and listings of programs have been described.[4,9] A summary of crystal data is given in Table 6.

CCDC reference number 186/1368.

See http://www.rsc.org/suppdata/dt/1999/1387/ for crystallographic files in .cif format.

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