# A deliberate approach for the syntheses of heterometallic supramolecules containing dimolybdenum $Mo_2^{4+}$ species coordinated to other metal units†

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Two compounds with quadruply bonded $Mo_2^{4+}$ species having isonicotinate ligands bound through the carboxylate group have been designed to act as anglers by luring metal-containing Lewis acids to bind to the N-pyridyl group. The corner pieces are $Mo_2(DAniF)_3(O_2CC_5H_4N)$ (**1**) and *cis*-$Mo_2(DAniF)_2(O_2CC_5H_4N)_2$ (**2**), DAniF = *N*,*N*′-di(*p*-anisyl)formamidinate. The heterometallic molecular rods **1**-Ni(acac)$_2$-**1** (**3**) and **1**-$Rh_2(O_2CCH_3)_4$-**1** (**4**) were made by reaction of **1** with Ni(acac)$_2$ and the metal–metal bonded species $Rh_2(O_2CCH_3)_4$, respectively. In these compounds either a mononuclear or a dinuclear species are sandwiched between two molecules of **1**. The cisoid compound **2** has been employed for the synthesis of a molecular rhombus, [**2**-Zn(Cl$_2$)]$_2$ (**5**). The successful syntheses and isolation of **3–5** show that the use of corner pieces with angler groups is an excellent approach for making heterometallic supramolecular compounds having a combination of metal–metal bonded units and other metal species.

## Introduction

The use of coordination bonds and weak interactions for the creation of extended arrays containing metal units connected by organic linkers is of great importance.[1] In metal-based supramolecules and nanostructures, the metal units play an important role in extending the dimensions of the molecules, controlling the structural geometries and tuning the chemical and physical properties of the compounds.[2,3] The basic strategy for the formation of discrete molecules or molecular assemblies with desirable size, shape and topology is to manipulate the relationship between the metal unit and organic linker using basic principles of transition metal chemistry[4] with the idea of developing functionalized molecules or molecular aggregates. Indeed, elegant design and synthesis have resulted in metal–ligand hybrid molecules that show potential applications as electronic devices and materials, for example, single molecular transistors[5] and single molecule magnets,[6] which are desirable because of their conducting,[7] magnetic[7c,8] and optical properties.[9]

Contrary to the synthesis of organic compounds with multiple functional groups that can be achieved with high specificity by use of well-defined reactions and reagents, creation of large metal-based molecules with a high degree of complexity remains highly challenging because of the dynamic properties and lability of many coordination bonds. A self-assembly approach could be an efficient way to achieve an ordered structure, but such an approach depends largely on the availability of programmed metal-based building blocks but these are generally rare.

In recent years, we have been able to create extended supramolecular architectures through convergent synthesis[10,11] by employing covalently bonded building blocks having dimetal units with a hierarchy of ligand labilities, such as those of the types $[M_2(DAniF)_n(NCCH_3)_{2(4-n)}]^{(4-n)+}$ and $M_2(DAniF)_n(O_2CCH_3)_{4-n}$ (M = Mo,[12,13] Rh[14] or Ru,[15] and DAniF = *N*,*N*′-di(*p*-anisyl)formamidinate). In a few of these compounds there are different metal units involved, for example, $[Mo_2(DAniF)_3]_2(OCH_3)_2$-$M(CH_3O)_2[Mo_2(DAniF)_3]$ (M = Zn and Co)[16] and $[Mo_2(DAniF)_3]_2(O_2MO_2)[Mo_2(DAniF)_3]$ (M = Mo and W).[17]

The latter are examples of rare heterometallic superstructures that may have potential applications as molecular devices[18] in addition to their interest in fundamental chemistry. In this report a deliberate synthesis for compounds having metal–metal bonded units combined with single metal or other dimetal units that help increase structural diversity is presented. In this "ligand-directed" approach, a functionalized ligand is used to generate various metal nuclearities. In the designed corner pieces, $Mo_2(DAniF)_3(O_2CC_5H_4N)$ (**1**) and *cis*-$Mo_2(DAniF)_2(O_2CC_5H_4N)_2$ (**2**), either one or two bifunctional isonicotinate ligands, $[O_2CC_5H_4N]^-$, are incorporated. The carboxylate group binds to the dimolybdenum unit and the tethered pyridyl nitrogen donor atom acts as the hook in a fishing pole to attract and then bind to other metal centers (**I** in Scheme 1). Thus the isonicotinate group may act as an *adapter* between dimetal units and single metal, or other dimetal species. A reported example that used a similar approach was that of the dirhenium building block *cis*-$[Re_2(dppm)_2(O_2CC_5H_4N)_2]$, prepared for the syntheses of heterometallic oligomers.[19]

The building blocks **1** and **2** are programmed to incorporate different metal units through a binary assembly reaction. Because of geometric constraint in each precursor, the resultant aggregates have predictable structural motifs. The heterometallic

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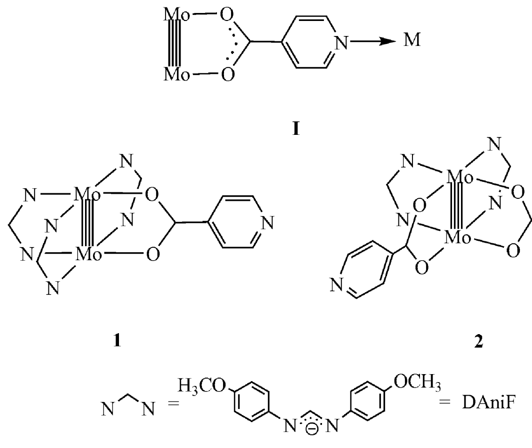
‡ Dedicated to the memory of Al Cotton, a wonderful friend, brilliant scientist and caring mentor whose life was cut short.



**Scheme 1**

supramolecules synthesized by self-assembly of **1** with selected metal complexes include two molecular rods, **1**-Ni(acac)$_2$-**1** (**3**) and **1**-Rh$_2$(O$_2$CCH$_3$)$_4$-**1** (**4**). Using the cisoid compound **2** as starting material, a molecular rhombus, [**2**-Zn(Cl$_2$)]$_2$ (**5**) was made. All these compounds have been structurally characterized using X-ray crystallography.

## Results and discussion

### Syntheses of dimolybdenum building blocks

The mixed-ligand, quadruply bonded paddlewheel complexes **1** and **2** were prepared at room temperature by ligand substitution reactions from the precursors $Mo_2(DAniF)_3(O_2CCH_3)$ and [*cis*-$Mo_2(DAniF)_2(NCCH_3)_4](BF_4)_2$, respectively, according to eqn (1) and (2).

$$Mo_2(DAniF)_3(O_2CCH_3) + HO_2CC_5H_4N \quad (1)$$

$$\xrightarrow[\text{rt}]{\text{NaOCH}_3/\text{THF}} Mo_2(DAniF)_3(O_2C_5H_4N)$$

$$cis\text{-}[Mo_2(DAniF)_2(NCCH_3)_4]^{2+} + 2HO_2CC_5H_4N \quad (2)$$

$$\xrightarrow[\text{rt}]{\text{NaOCH}_3} cis\text{-}[Mo_2(DAniF)_2(O_2CC_5H_4N)_2]$$

The first equation represents a two step process. In this reaction replacement of the acetate group in $Mo_2(DAniF)_3(O_2CCH_3)$ by an isonicotinate ligand is needed. Because both of the leaving and incoming groups are carboxylates, direct ligand exchange is generally inefficient, as shown for example during the conversion of *cis*-$ReCl_2(\mu\text{-dppm})_2(O_2CCH_3)_2$ into *cis*-$ReCl_2(\mu\text{-dppm})_2(O_2CC_5H_4N)_2$, which required reflux of the reaction mixture over a period of two days.[19] The carboxylate replacement process has now been improved by using $NaOCH_3$ to remove the acetate group in a reaction that forms the intermediate compound $Mo_2(DAniF)_3(OCH_3)(CH_3OH)$,[20] which was then treated with neutral isonicotinic acid. This intermediary does not have to be isolated nor purified, and this two-step, one-pot reaction gives the monodentate building block **1** in good yield.

Substitution of acetonitrile molecules in [*cis*-$Mo_2(DAniF)_2(NCCH_3)_4]^{2+}$ by isonicotinate groups for the preparation of **2** is convenient and straightforward because of the high lability of the $CH_3CN$ molecules. In principle, this reaction resembles that for the preparation of *cis*-$Mo_2(DAniF)_2(O_2CCH_3)_2$, made by mixing the precursor with an excess of sodium acetate.[21] For the synthesis of **2**, the isonicotinate anion was generated *in situ* by addition of sodium methoxide to a mixture of the dimolybdenum precursor and nicotinic acid in acetonitrile. The neutral corner piece **2**, which has a low solubility in polar solvents, readily precipitates from the reaction mixture. Compound **2** appears to be stable and there is no evidence for a *cis* to *trans* isomerization.

The two corner pieces **1** and **2** are isolated in good purity as shown by their $^1$H NMR spectra in $CDCl_3$. For **1**, there are two singlets at 8.54 and 8.44 ppm in a ratio of 1 : 2 that correspond to the methine protons from the formamidinate ligands *trans* and *cis* to the isonicotinate group, respectively. The aromatic protons from the isonicotinate ligands are deshielded, and appear at low field as two apparent doublets, one centered at 8.78 ppm and the other one at 8.11 ppm. The aromatic protons from the two types of hydrogen atoms of the anisyl groups appear as two sets of signals, one for the groups *cis* to the isonicotinate group and the other one for the *trans* protons. These appear as pseudo doublets centered at 6.51 and 6.28 ppm, and 6.68 and 6.59 ppm, respectively. Finally, the signals for the methoxy groups of the anisyl groups appear as singlets at 3.76 (12 H) and 3.70 (6 H). The UV-vis absorption at 464 nm ($2.4 \times 10^4$ $M^{-1}$ $cm^{-1}$) is within the range of the $\delta \rightarrow \delta^*$ transitions in quadruply bonded compounds of this type.[22] The $^1$H NMR spectrum of **2** in $CDCl_3$ suggests the presence of a highly symmetrical species in solution. There are two signals (centered at 8.75 and 8.04 ppm) for the two types of hydrogen atoms in the isonicotinate anion and only one singlet for the methine hydrogen atom at 8.44 ppm. The aromatic groups of the formamidinate groups are also equivalent and the signals centered at 6.63 ppm. A singlet at 3.72 ppm corresponds to the hydrogen atoms in the methoxy groups.

### Syntheses of large arrays

Because of the dangling pyridyl groups, the dimolybdenum building blocks **1** and **2** may be viewed as monodentate or bidentate ligands, respectively, capable of binding to another metal unit through a coordination bond. In both compounds the linker is preinstalled, *e.g.*, the pyridyl group $-C_5H_4N \rightarrow$ is attached to the $Mo_2^{4+}$ unit and is accessible to bind a Lewis acid. With these preprogrammed building blocks, heterometallic supramolecules can be prepared by efficient and straightforward binary self-assembly reactions. Compound **1** has been used for the preparation of hybrid molecules having three discrete metal centers, and the corner piece **2** in combination with a single metal unit $ZnCl_2$ for the preparation of a molecular rhombus.

By mixing **1** and $Ni(acac)_2$ in a 2 : 1 stoichiometric ratio at ambient temperature compound **3** is prepared in reasonable yield. Likewise reaction of **1** with strong Lewis acids having $Rh_2^{4+}$ paddlewheel cores such as dirhodium tetraacetate leads to the formation of **4**, in which an $Rh_2^{4+}$ unit is located between two dimolybdenum units. Both **3** and **4** are rod-like molecules (*vide infra*).

Because of its ligand arrangement, the corner piece **2** is expected to give molecules having different geometries than those from reactions using **1**. In a reaction with the tetrahedrally coordinated $ZnCl_2(THF)_2$ species and **2**, the labile THF molecules were easily replaced by the dangling N-donor pyridyl groups to generate a cyclic heterometallic oligomer **5** having the shape of a rhombus.[23]

All the assembled molecules (**3**, **4** and **5**) are neutral. Their solubility is generally low in polar solvents, such as ethanol and acetonitrile, but fairly high in dichloromethane. This difference in solubility in polar and non polar solvents is helpful for product purification and crystal growth, and facilitates product characterization in both solid state and in solution.

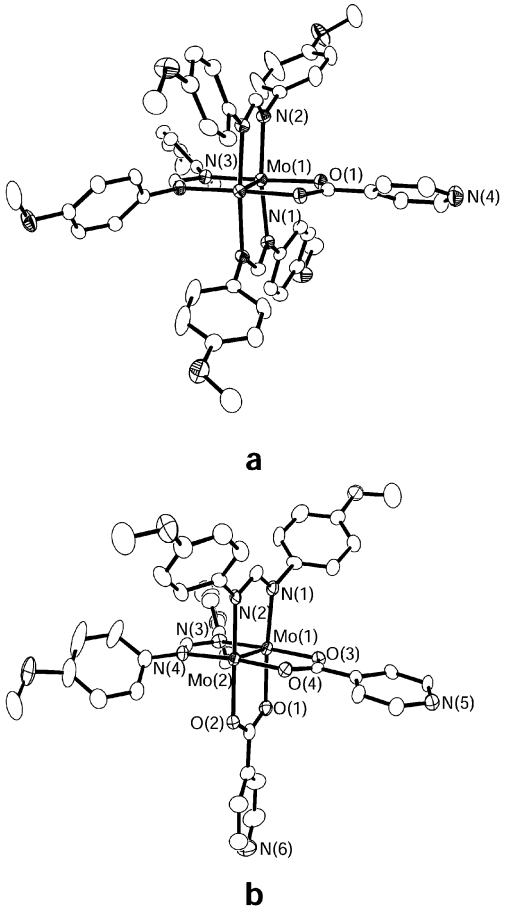


**Fig. 2** Molecular structures of the building blocks **1** (a) and **2** (b). Displacement ellipsoids are drawn at the 40% probability level. All hydrogen atoms have been omitted for clarity.

## Structures

As shown in Fig. 1a, compound **1** has a quadruply bonded $Mo_2^{4+}$ unit equatorially coordinated by three formamidinate (DAniF) ligands and one isonicotinate ($O_2CC_5H_4N$) group that is coordinated to the dimetal unit through the carboxylate terminus. This arrangement leaves a dangling pyridyl moiety capable of serving as an angler for the capture of metal-containing Lewis acids. The Mo–Mo bond distance, 2.0906(5) Å, is typical for quadruply bonded dimolybdenum units embraced by four, three-atom bridging ligands, such as $Mo_2(DAniF)_4$[24] and $Mo_2(OCCH_3)_4$.[25] As designed, this molecule is closely related to that of its precursor $Mo_2(DAniF)_3(O_2CCH_3)$ by having the same coordination sphere and a similar Mo–Mo bond length (2.0892(8) Å).[12] Upon replacement of the acetate by an isonicotinate group, the color of the compounds changes from yellow to red as the $\delta \rightarrow \delta^*$ transition is shifted from 439 nm to 464 nm. In the solid state, the pyridyl group is not in the plane defined by the dimetal unit and the $CO_2$ bridging group; the torsion angle is about 24°.

In **2** there are two cisoid DAniF and two isonicotinate anions surrounding the $Mo_2^{4+}$ unit, as illustrated in Fig. 1b. The Mo–Mo bond length, 2.115(2) Å, is 0.02 Å longer than that of 2.092(2) Å in *cis*-$Mo_2(DAniF)_2(O_2CCH_3)_2$,[21] a molecule with a similar core. Even though this bond length is slightly elongated, the distance falls in the range of dimolybdenum quadruply bonded distances.[22,26] The two orthogonal pyridyl groups are slightly tilted relative to the five-membered chelating rings $\overline{\text{O–Mo–Mo–O–C}}$ and the torsion angles are 5.90° and 14.45°.

The rod-like compound **3** may be described by the formula **1**-Ni(acac)$_2$-**1**. The two $Mo_2^{4+}$ units are connected through isonicotinate termini to a planar Ni(acac)$_2$ unit as shown in Fig. 2. This compound crystallized in the space group $P\bar{1}$ with the molecule residing on a general position. Because the isonicotinate linkers are slightly bent the molecule is slightly curved. This hybrid rod is long when compared to other "dimers of dimers" synthesized using the $[Mo_2(DAniF)_3]^+$ building block. The distance between the two dimetal centers is about 18 Å. The longest $Mo_2 \cdots Mo_2$ separation, about 16 Å, was reported in a compound having the conjugated dicarboxylate linker, deca-2,4,6,8-*trans*,*trans*,*trans*,*trans*-octatetraene-1,10-dioate.[27] In **3**, the two crystallographically independent Mo–Mo bonds are chemically equivalent (bond lengths of 2.0927(7) and 2.0923(7) Å) and

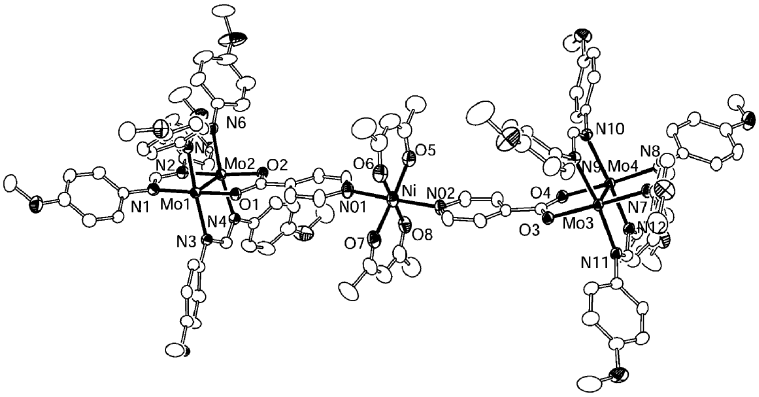


**Fig. 1** Molecular structure of **3** in **3**·$2CH_2Cl_2$ drawn with displacement ellipsoids at the 40% probability level. All hydrogen atoms have been omitted for clarity.

are essentially parallel to each other. The two pyridyl groups on the apices of the octahedrally coordinated $Ni^{2+}$ moiety are essentially co-planar and mutually define a plane that bisects the $NiO_4$ square. The torsion angles (*ca.* 2°) between each of the pyridyl rings and the corresponding $\overline{\mathrm{O{-}Mo{-}Mo{-}O{-}C}}$ groups are significantly smaller than in **1** (*ca.* 24°).

The rod **4**, described by the formula **1**-$Rh_2(O_2CCH_3)_4$-**1**, crystallized in the triclinic $P\bar{1}$ space group with $Z = 1$. This molecule has an inversion center at the midpoint of the Rh–Rh bond. As shown in Fig. 3, there are two basically parallel $Mo_2^{4+}$ units at the ends of the rod. A central $Rh_2^{4+}$ unit has the dirhodium single bond essentially perpendicular to the dimolybdenum units. The separation between the two $Mo_2^{4+}$ units of about 21 Å is the longest among all dimolybdenum pairs synthesized to date. The crystallographically independent Mo–Mo bond distance, 2.0925(8) Å, is almost identical to those in **1** and **3** (Table 1). The Rh–Rh bond length of 2.402(1) Å and the Rh–N distance of 2.240(4) Å are comparable to those in $Rh_2(O_2CCH_3)_4(py)_2$.[28] The molecule has a highly symmetrical arrangement having idealized $D_{2h}$ symmetry. The two pyridyl groups have torsion angles of 5.5°, much smaller than that of 24° in the building block **1**.

In compound **5**, $Zn^{2+}$ moieties serve as linkers between the cisoid $Mo_2^{4+}$ units. The compound crystallized in the space group $P2_1/n$. In each unit cell, there are two crystallographically independent molecules residing on special positions. This supramolecule is a distorted rhombus with alternating $Zn^{2+}$ and $Mo_2^{4+}$ metal units at the vertices and four isonicotinate groups serving as edges (Fig. 4). The formula may be abbreviated as $[\mathbf{2}\text{-}ZnCl_2]_2$. The Mo–Mo distances of 2.0920(7) Å are slightly shorter than in the building block **2** but similar to those in **1**, **3** and **4**. The Zn · · · Zn separation of 11.935 Å is shorter than the other diagonal length, 13.475 Å, measured from the centers of the two $Mo_2^{4+}$ units. The geometry

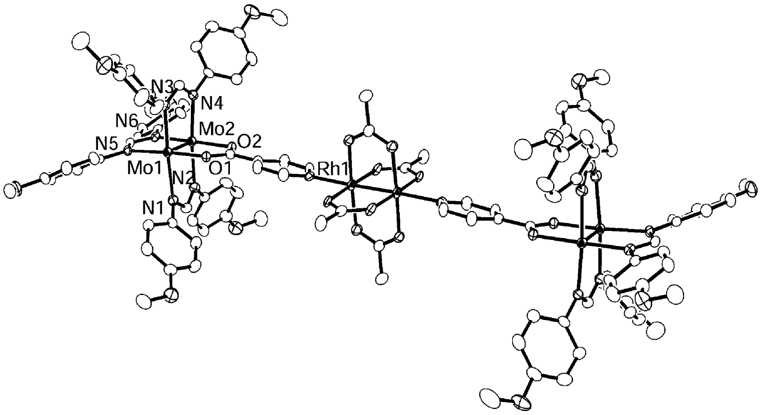


**Fig. 3** Molecular structure of **4** in **4**·$4.5CH_2Cl_2 \cdot C_6H_{14}$. Displacement ellipsoids are drawn at the 40% probability level. All hydrogen atoms have been omitted for clarity.

**Table 1** Selected bond lengths (Å) and angles (°) for **1–5**

| | **1** | **2**·$2CH_2Cl_2$ | **3**·$2CH_2Cl_2$ | **4**·$4.5CH_2Cl_2 \cdot C_6H_{14}$ | **5**·$4CH_2Cl_2$ |
|---|---|---|---|---|---|
| Mo(1)–Mo(2) | | 2.1153(17) | 2.0925(8) | 2.0926(8) | 2.0920(7) |
| Mo(1)–Mo(1A) | 2.0905(5) | | | | |
| Mo(3)–Mo(4) | | | 2.0923(7) | | |
| Mo(1)–N(1) | 2.1470(19) | 2.103(11) | 2.109(3) | 2.142(4) | 2.109(4) |
| Mo(1)–N(3) | 2.123(2) | 2.110(10) | 2.139(3) | 2.162(4) | 2.104(4) |
| Mo(1)–N(5) | | | 2.137(3) | 2.161(5) | |
| Mo(2)–N(2) | | 2.105(10) | 2.138(3) | 2.133(4) | 2.118(3) |
| Mo(2)–N(4) | | 2.120(10) | 2.136(3) | 2.123(4) | 2.114(4) |
| Mo(2)–N(6) | | | 2.169(3) | 2.161(4) | |
| Mo(1)–O(1) | 2.1454(17) | 2.127(9) | 2.144(3) | 2.137(3) | 2.123(3) |
| Mo(1)–O(3) | | 2.139(8) | | | 2.149(3) |
| Mo(2)–O(2) | | 2.140(8) | 2.124(3) | 2.148(3) | 2.136(3) |
| Mo(2)–O(4) | | 2.138(8) | | | 2.111(3) |
| N(1)–Mo(1)–O(1) | 85.73(7) | 175.4(4) | 174.26(12) | 87.96(14) | 174.72(12) |
| N(3)–Mo(1)–O(1) | 175.23(6) | 88.7(4) | 88.02(11) | 175.33(14) | 85.26(13) |
| N(5)–Mo(1)–O(1) | | | | 84.04(15) | |
| N(2)–Mo(2)–O(2) | | 174.1(4) | 174.24(13) | 88.54(14) | 175.64(12) |
| N(4)–Mo(2)–O(2) | | 89.4(4) | 85.10(11) | 174.14(15) | 87.27(13) |
| N(6)–Mo(2)–O(2) | | | 86.45(11) | 88.26(15) | |
| N(1)–Mo(1)–N(3) | | 94.6(4) | 88.60(13) | 94.02(15) | 95.32(14) |
| N(1)–Mo(1)–N(5) | | | 95.38(13) | 170.34(16) | |
| N(2)–Mo(2)–N(4) | | 93.9(4) | 90.87(13) | 93.62(15) | 95.28(13) |
| N(2)–Mo(2)–N(6) | | | 97.19(13) | 174.23(17) | |
| O(1)–Mo(1)–O(3) | | 88.5(3) | | | 85.92(12) |
| O(2)–Mo(2)–O(4) | | | | | 86.49(12) |

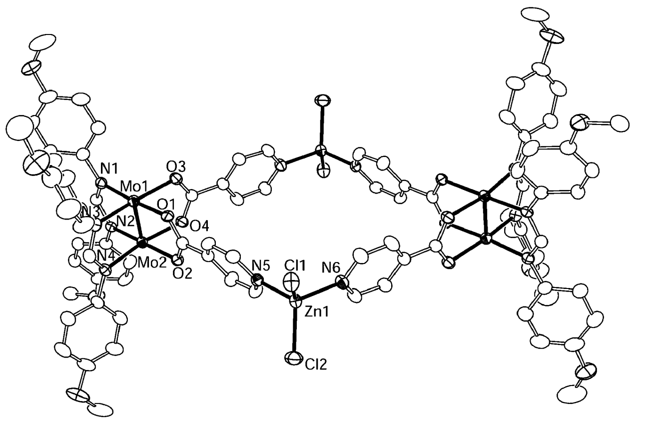


**Fig. 4** Molecular structure of **5** in **5**·4$CH_2Cl_2$ drawn with displacement ellipsoids at the 40% probability level. All hydrogen atoms have been omitted for clarity.

for the $ZnCl_2N_2$ moiety is that of a distorted tetrahedron. The N–Zn–N angle, 102.8°, is slightly smaller than the ideal value of 109.5°. While the Cl–Zn–Cl angle, 119.63(8)° is larger. The molecule defines a diamond shaped area with an approximate dimension of 9 Å × 9 Å and hosts one interstitial dichloromethane molecule disordered over two orientations.

Information on the structures in solution of these large molecules has been obtained by $^1$H NMR spectroscopy. Compounds **4** and **5** are diamagnetic because of the presence of two quadruply bonded $Mo_2^{4+}$ units and the singly bonded $Rh_2^{4+}$ unit in **4** and the $d^{10}$ electronic structure of the $Zn^{2+}$ units in **5**. For the rod-like **4**, the spectrum in $CDCl_3$ shows a singlet at 8.59 ppm corresponding to the methine hydrogen atoms from the formamidinate ligands *trans* to the isonicotinate ligands. The signals for the *cis* methine ligands overlap with some of the isonicotinate signals at 8.46 ppm while the other signals for the isonicotinate are centered at 9.48 ppm. The rest of the signals, including the singlet at 1.96 ppm for the methyl groups from the $Rh_2(O_2CCH_3)_4$ moiety, are in the expected regions of the spectrum for a highly symmetrical species. Therefore the spectrum is consistent with the solid state structure. Similarly for **5**, the simple pattern of the spectrum with only two singlets at 8.47 and 3.72 ppm for the methine and methoxy groups and the expected pattern for the aromatic hydrogen atoms indicate that the shape of the molecule in solution resembles that in the solid state.

Unlike **4** and **5**, compound **3** is paramagnetic with two unpaired electrons per molecule ($\mu_{\text{eff}}$ = 3.4 BM), as determined from bulk magnetic susceptibility measurements. The source of the paramagnetism is the octahedral coordination of the $Ni^{2+}$ ions derived from the coordination of the two pyridyl groups to the square planar $Ni(acac)_2$ moiety. Species with octahedral *trans*-$Ni(O)_4(N)_2$ units are typically paramagnetic as in *trans*-$Ni(acac)_2(amine)_2$ compounds for which the $\mu_{\text{eff}}$ have been reported to be in the range of 3.2–3.4 BM.[29] Despite the paramagnetism of **3**, its $^1$H NMR spectrum in $CD_3Cl$ shows mostly sharp signals in the expected regions of the spectra. For example, there are singlets with a ratio of 2 : 1 at 8.31 and 8.45 ppm for the methine and 3.71 and 3.64 ppm for methoxy protons, respectively, from the DAniF ligands. The signals for the anisyl groups are also as expected (6.17–6.60 ppm). However, close inspection of the spectrum shows that the signals from the ligands directly bound to the $Ni^{2+}$ unit are absent. Even when the spectral window was opened to cover the region between −150 ppm and +150 ppm, signals from the acac methyl groups and from the isonicotinate groups were absent. The sharpness of the signals from the anisyl groups and the absence of those in the $Ni^{2+}$ units suggest that there is little or no electronic communication through the isonicotinate bridge, consistent with the electrochemical data below.

## Electrochemistry

Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) for **1–5** were measured in $CH_2Cl_2$ solutions. The corner pieces **1** and **2** show reversible one-electron redox processes at 310 and 560 mV *vs.* Ag/AgCl, respectively (Fig. 5). Previous studies on *dimer of dimers* have shown that the separation between the two $Mo_2$ units is a very important factor in determining whether electronic communication is efficient or not.[27] As the intermetal separations increase, it has often been observed that electronic communication decreases according to an exponential law.[30] Because the separations between the $Mo_2$ units in **3** and **4** are the longest known for any *dimer of dimers* compounds of this type, an extremely weak communication may be anticipated. This is consistent with the electrochemical data (see Fig. 5). Compounds **3** and **4** show very similar patterns in the CVs and DPVs, a redox wave was observed for each one of them between 300 and 400 mV. By analogy to the *dimer of dimers* linked by long unsaturated dicarboxylate ligands,[31] this wave can be assigned to the two unresolved one-electron oxidation processes on each of the dimolybdenum units. The CV for the rhombohedral compound **5** appears to correspond to a less reversible process. It is possible that because of a relatively weak N to Zn interaction, the molecule may decompose upon oxidation.

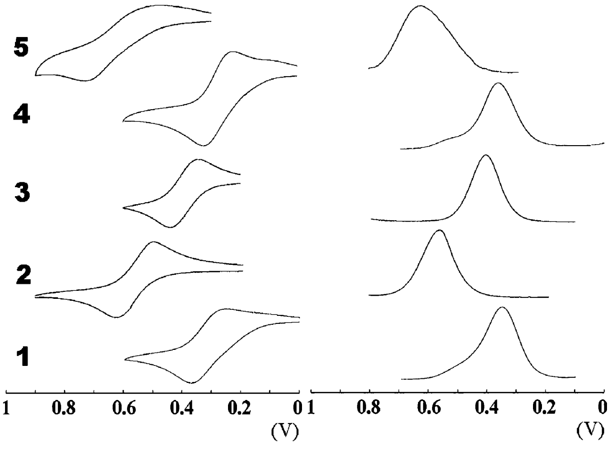


**Fig. 5** CVs and DPVs (potentials *vs* Ag/AgCl, in $CH_2Cl_2$) for compounds **1–5**.

## Conclusions

Two new dimolybdenum-containing building blocks $Mo_2(DAniF)_3(O_2C_5H_4N)$ (**1**) and *cis*-$Mo_2(DAniF)_2(O_2CH_4N)_2$ (**2**), each having an angler composed of a pyridyl group capable of binding to metal-containing Lewis acids, have been synthesized. The functionalization by introduction of a bi-functional isonicotinate ligand allows incorporation into **1** and **2** of other metal centers *via* coordination bonds and the formation of heterometallic supramolecules. By taking advantage of these two programmed building blocks, spontaneous self-assemblies with selective metal complexes, *e.g.*, Ni(acac)$_2$, Rh$_2$(O$_2$CCH$_3$)$_4$ and Zn$_2$Cl$_2$, formation of two metal-based molecular rods **1**-Ni(acac)$_2$-**1** (**3**), **1**-Rh$_2$(O$_2$CCH$_3$)$_4$-**1** (**4**), and a cyclic oligomer [**2**-Zn$_2$Cl$_2$]$_2$ (**5**) have been synthesized. Compounds **3** and **4** are longer than any previously reported dimolybdenum pair. Meanwhile the rhombohedral molecule **5** has a large cavity which holds a CH$_2$Cl$_2$ guest molecule. Incorporation of different metal units into structurally defined architectures is a way to modify the molecular architecture and tune chemical and physical properties. The preparative concept and methodology developed here should have general application for the synthesis of heteronuclear species having metal–metal corner pieces bound to metal-containing Lewis acids.

## Experimental

### Materials and methods

All manipulations and procedures were performed under a nitrogen atmosphere, using either a nitrogen drybox or standard Schlenk line techniques. Solvents were purified under argon using a Glass Contour solvent purification system or distilled over appropriate drying agents under nitrogen. The starting materials Mo$_2$(DAniF)$_3$(O$_2$CCH$_3$)[12] and [*cis*-Mo$_2$(DAniF)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$[13] were prepared following reported procedures. The dirhodium compound Rh$_2$(O$_2$CCH$_3$)$_4$(NCCH$_3$)$_2$ was prepared by treating Rh$_2$(O$_2$CCH$_3$)$_4$,[32] with acetonitrile. Commercially available chemicals were used as received.

### Physical measurements

Elemental analyses were performed by Robertson Microlit Laboratories, Madison, New Jersey. Electronic spectra were measured in CH$_2$Cl$_2$ solution at ambient temperature on a Shimadzu UV-2501PC spectrometer. $^1$H NMR spectra were recorded on an Inova-300 or Mercury NMR spectrometer with chemical shifts ($\delta$, ppm) referenced to CDCl$_3$. Cyclic voltammograms and differential pulse voltammograms were collected on a CH Instruments electrochemical analyzer with Pt working and auxiliary electrodes, Ag/AgCl reference electrode, scan rate (for CV) of 100 mV s$^{-1}$, and 0.10 M Bu$_4$NPF$_6$ (in CH$_2$Cl$_2$) as electrolyte.

**Preparation of Mo$_2$(DAniF)$_3$(O$_2$CC$_5$H$_4$N), 1.** To a yellow solution of Mo$_2$(DAniF)$_3$(O$_2$CCH$_3$) (0.512 g, 0.500 mmol) in 15 mL of THF, was added 1.0 mL of a NaOCH$_3$ solution (0.5 M in methanol). After stirring for about 2 h, a colorless microcrystalline material, presumably sodium acetate, was removed by filtration. To the filtrate was added an excess of isonicotinic acid (0.080 g, 0.650 mmol). Upon stirring, the color of the mixture immediately changed from yellow to red. After stirring at room temperature for an additional half hour, the solvent was removed under vacuum, and the residue was washed with ethanol (2 × 15 mL), and then dried under vacuum. The red solid was dissolved in dichloromethane (15 mL) and the solution was layered with hexanes. Red block-shaped crystals formed after one day. Yield: 0.380 g (70%). $^1$H NMR (CDCl$_3$, ppm): 8.78 (d, 2H, isonicotinate), 8.54 (s, 1H, –NC*H*N–), 8.44 (s, 2H, –NC*H*N–), 8.11 (d, 2H, isonicotinate), 6.68 (d, 8H, aromatic), 6.59 (d, 8H, aromatic), 6.51 (d, 4H, aromatic), 6.28 (d, 4H, aromatic), 3.76 (s, 12H, –OC*H*$_3$), 3.70 (s, 6H, –OC*H*$_3$). UV-vis, $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 464 nm (2.4 × 10$^4$). Anal. Calcd. for C$_{51}$H$_{49}$Mo$_2$N$_7$O$_8$: C, 56.72; H, 4.57; N, 9.08. Found: C, 56.49; H, 4.86; N, 9.29.

**Preparation of *cis*-Mo$_2$(DAniF)$_2$(O$_2$CC$_5$H$_4$N)$_2$, 2.** A mixture of [*cis*-Mo$_2$(DAniF)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ (0.520 g, 0.500 mmol) and isonicotinic acid (0.170 mg, 1.38 mmol) was placed in a Schlenk flask. With stirring acetonitrile (*ca.* 20 mL) was added to the solid, producing a blue solution. After about 10 min, 2.0 mL of a sodium methoxide solution (0.5 M in methanol) was added. The color changed from blue to red. The reaction mixture was allowed to stir at room temperature for 3 h. During this period a dark red precipitate formed. The supernatant solution was then decanted. The red solid was washed with 20 mL of ethanol and then dried under vacuum. The crude product was dissolved in dichloromethane (15 mL) and the solution was layered with hexanes. Red needle-shaped crystals formed after 2 days. Yield: 0.24 g (56%). $^1$H NMR (CDCl$_3$, ppm): 8.75 (d, 4H, isonicotinate), 8.44 (s, 2H, –NC*H*N–), 8.04 (d, 4H, isonicotinate), 6.63 (m, 16H, aromatic), 3.72 (s, 12H, –OC*H*$_3$). UV-vis, $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 450 nm (1.2 × 10$^4$). Anal. Calcd. for C$_{42.3}$H$_{38.6}$Cl$_{0.6}$Mo$_2$N$_6$O$_8$(**2**·0.3CH$_2$Cl$_2$): C, 52.26; H, 4.04; N, 8.64. Found: C, 52.23; H, 3.66; N, 8.78.

**Preparation of [Mo$_2$(DAniF)$_3$(O$_2$CC$_5$H$_4$N)]$_2$Ni(C$_5$H$_7$O$_2$)$_2$, 3.** The dimolybdenum building block Mo$_2$(DAniF)$_3$(O$_2$CC$_5$H$_4$N) (**1**) (0.400 g, 0.400 mmol) was dissolved in 20 mL of THF. The resulting brownish red solution was transferred into a flask containing Ni(acac)$_2$ (0.050 g, 0.20 mmol), generating a bright red solution. After the reaction mixture was stirred for an additional 2 h, the solvent was removed under reduced pressure. The red residue was washed with ethanol (*ca.* 15 mL) followed by hexanes (*ca.*10 mL). The dry solid was dissolved in about 15 mL of dichloromethane and the solution was layered with 40 mL of hexanes, affording red block-shaped crystals after a few days. Yield: 0.285 g (24%). $^1$H NMR (CDCl$_3$, ppm): 8.54 (s, 2H, –NC*H*N–), 8.31 (s, 4H, –NC*H*N–), 6.60 (d, 16H, aromatic), 6.41 (d, 24H, aromatic), 6.17 (d, 8H, aromatic), 3.71 (s, 24H, –OC*H*$_3$), 3.64 (s, 12H, –OC*H*$_3$). UV-vis, $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ mol$^{-1}$): 474 nm (2.5 × 10$^4$). $\mu_{eff}$ = 3.4 BM. Anal. Calcd. for C$_{115}$H$_{118}$Cl$_6$Mo$_4$N$_{14}$O$_{20}$Ni (**3**·3CH$_2$Cl$_2$): C, 51.70; H, 4.45; N, 7.34. Found: C, 51.33; H, 4.62; N, 7.40.

**Preparation of [Mo$_2$(DAniF)$_3$(O$_2$CC$_5$H$_4$N)]$_2$[Rh$_2$(O$_2$CCH$_3$)$_4$], 4.** A solution of purple Rh$_2$(O$_2$CCH$_3$)$_4$(NCCH$_3$)$_2$ (0.052 g, 0.100 mmol) and red **1** (0.216 g, 0.200 mmol) was prepared in 20 mL of acetonitrile. The reaction mixture was allowed to stir at room temperature for 4 h. A dark red precipitate formed. The solvent was then removed under reduced pressure. The dark red residue was washed with ethanol (2 × 15 mL). The crude product was dissolved in 15 mL of dichloromethane and the solution was layered with 40 mL of hexanes, affording dark red crystals after one day. Yield: 0.08 g (31%). $^1$H NMR (CDCl$_3$, ppm): 9.48 (s, 4H, isonicotinate), 8.59 (s, 2H, –NC*H*N–), 8.46 (s, 8H, –NC*H*N– and isonicotinate) 6.72 (d, 16H, aromatic), 6.62 (d, 16H, aromatic), 6.54 (d, 8H, aromatic), 6.33 (d, 8H, aromatic), 3.78 (s, 24H, –OC*H*$_3$), 3.73 (s, 12H, –OC*H*$_3$), 1.96 (s, 12H, –C*H*$_3$). UV-vis, $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 499 nm (4.1 × 10$^4$). Anal. Calcd.

**Table 2** X-Ray crystallographic data for **1–5**

| Compound | **1** | **2**·2CH$_2$Cl$_2$ | **3**·2CH$_2$Cl$_2$ | **4**·4.5CH$_2$Cl$_2$·C$_6$H$_{14}$ | **5**·4CH$_2$Cl$_2$ |
|---|---|---|---|---|---|
| Empirical formula | $C_{51}H_{49}Mo_2N_7O_8$ | $C_{44}H_{42}Cl_4 Mo_2N_6O_8$ | $C_{114}H_{116}Cl_4Mo_4N_{14}O_{20}Ni$ | $C_{120.5}H_{130}Cl_9Mo_4N_{14}O_{24}Rh_2$ | $C_{88}H_{84}Cl_{12}Mo_4 N_{12}O_{16}Zn_2$ |
| FW | 1079.85 | 1116.52 | 2586.47 | 3067.02 | 2505.57 |
| Space group | *C*2/*c* (No. 15) | *Pbca* (No. 61) | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | $P2_1/n$ (No. 14) |
| $a$/Å | 17.615(3) | 13.942(7) | 14.966(5) | 15.260(4) | 10.588(3) |
| $b$/Å | 18.492(3) | 19.406(10) | 17.526(6) | 16.014(5) | 20.103(6) |
| $c$/Å | 16.855(3) | 35.947(18) | 23.141(9) | 16.228(5) | 24.879(8) |
| $\alpha$/° | 90 | 90 | 102.989(7) | 108.216(5) | 90 |
| $\beta$/° | 118.286(4) | 90 | 98.259(7) | 102.413(5) | 94.073(5) |
| $\gamma$/° | 90 | 90 | 90.533(7) | 106.435(5) | 90 |
| $V$/Å$^3$ | 4834.7(16) | 9726(8) | 5848(4) | 3406.8(17) | 5282(3) |
| $Z$ | 4 | 8 | 2 | 1 | 2 |
| $T$/K | 213 | 213 | 213 | 213 | 213 |
| $d_{calcd}$/g cm$^{-3}$ | 1.484 | 1.525 | 1.469 | 1.495 | 1.575 |
| $\mu$/mm$^{-1}$ | 0.580 | 0.791 | 0.738 | 0.840 | 1.275 |
| $R1^a$ ($wR2^b$) | 0.0453 (0.0798) | 0.1264 (0.1816) | 0.0817 (0.1380) | 0.0847 (0.1588) | 0.0625 (0.1194) |

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

for $C_{110}H_{110}Mo_4N_{14}O_{24}Rh_2$: C, 50.78; H, 4.26; N, 7.53. Found: C, 50.51; H, 4.10; N, 7.72.

**Preparation of [*cis*-Mo$_2$(DAniF)$_2$(O$_2$CC$_5$H$_4$N)$_2$][ZnCl$_2$]$_2$, 5.** The dimolybdenum building block *cis*-Mo$_2$(DAniF)$_2$(O$_2$CC$_5$H$_4$N)$_2$ (**2**) (0.095 g, 0.100 mmol) was mixed with anhydrous ZnCl$_2$ (0.050 g, 0.37 mmol) in 20 mL of THF. The reaction mixture was stirred for 2 h, during which time a red–purple precipitate formed. The supernatant solution was decanted and the residue was dried under vacuum. The solid was then extracted with *ca.* 15 mL of dichloromethane and the mixture filtered through a Celite-packed frit. The filtrate was layered with 30 mL of hexanes. Dark red needle-shaped crystals formed after 4 days. Yield: 0.050 g (25%). $^1$H NMR (CDCl$_3$, ppm): 8.96 (s, 8H, isonicotinate), 8.47 (s, 4H, –NC*H*N–), 8.16 (s, 8H, isonicotinate), 6.60 (m, 32H, aromatic), 3.72 (s, 24H, –OC*H*$_3$). UV-vis, $\lambda_{max}$ ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 508 nm (4.3 × 10$^4$). Anal. Calcd. for $C_{86}H_{80}Cl_8Mo_4N_{12}O_{16}Zn_2$: C, 44.27; H, 3.45; N, 7.19. Found: C, 44.27; H, 3.52; N, 7.08.

### X-Ray structure determinations

Each crystal was mounted on a cryoloop and centered in the goniometer of a Bruker SMART 1000 CCD area detector diffractometer and then cooled to −60 °C. Cell parameters were determined using the program SMART.[33] Data reduction and integration were performed with the software package SAINT,[34] and absorption corrections were applied using the program SADABS.[35] In all structures, the positions of the heavy atoms were found *via* direct methods using the program SHELXTL.[36] Subsequent cycles of least-square refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were added in idealized positions. Non-hydrogen atoms were refined with anisotropic displacement parameters. Some of the anisyl group in the DAniF ligands and interstitial CH$_2$Cl$_2$ molecules were found disordered, and they were refined with soft constraints. Crystallographic data for **1**, **2**·2CH$_2$Cl$_2$, **3**·2CH$_2$Cl$_2$, **4**·4.5CH$_2$Cl$_2$·C$_6$H$_{14}$ and **5**·4CH$_2$Cl$_2$ are in Table 2, and selected bond distances and angles in Table 1.

CCDC reference numbers 628985–628989 for **1–5**, respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617932k

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