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A molecular loop with interstitial channels in a chiral environment: exploration of the chemistry of Mo_2^{4+} species with chiral and non-chiral dicarboxylate anions

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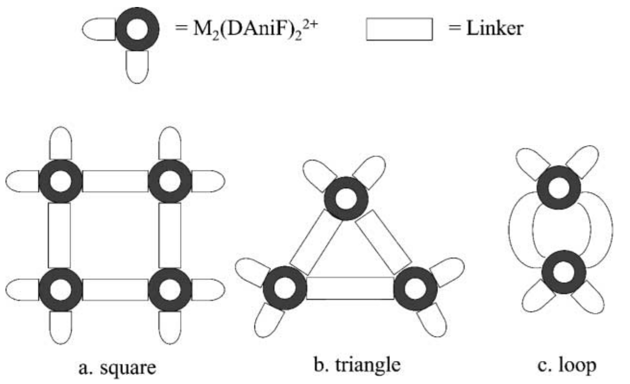
An enantiomericaly pure chiral loop containing two *cis*-$Mo_2(DAniF)_2^{2+}$ (DAniF = di-*p*-anisylformamidinate) units was obtained by reaction of *cis*-$[Mo_2(DAniF)_2(NCMe)_4](BF_4)_2$ with a chiral dicarboxylate which is easily prepared from hydroquinone and ethyl (*S*)-lactate. The compound crystallizes in the non-centrosymmetric *I*222 space group with molecules stacking so as to form channels capable of hosting guest molecules such as CH_2Cl_2. These properties of the compound, which has been synthesized in high yield, makes it promising for applications in stereoselective catalysis. Similar reactions with isomeric dicarboxylate linkers, as well as with some non-chiral ligands, were studied. The nature of the products depends on the bite angle of the ligand.

Introduction

Metal–metal-bonded compounds have proven useful in many areas, such as catalysis,[1] medicine[2] and for building supramolecular arrays.[3] Some of the most notable catalytic processes employ chiral ligands that induce optical activity in the products.[4] Chirality is also of great importance in medicine, as many processes, *e.g.* enzymatic processes,[5] are controlled by optically active centers. In the field of supramolecular chemistry, efforts have been made to study the use of chiral ligands attached to metal centers,[6] but structural characterization is often hampered by difficulties in crystallizing large chiral molecules.[7] Only two systems having chiral species bound to metal–metal-bonded centers have been structurally characterized. One of them is a triangle made with $Ru_2(CO)_4L_2$ (L = axial MeCN or PPh_3) corner pieces with optically active tartrate dianions as linkers.[8] The other is a set of molecular pairs containing two $Mo_2(DAniF)_3^+$ units (DAniF = *N*,*N*′-di-*p*-anisylformamidinate) bridged by either L-tartrate or D-aspartate.[9]

A useful type of dimetal unit in the construction of polygonal supramolecules is $M_2(DAniF)_2$ (M = Mo, Ru and Rh), which can form loops, triangles, squares or more complex entities,[10] depending on the nature of the linker and the presence or absence of axial ligation. For example, we have shown that $M_2(DAniF)_2$ corner pieces give squares with rigid dicarboxylate linkers, such as the dianion of terephthalic acid,[11] triangles with the less constrained 1,4-dicyclohexanedicarboxylate[12] and loops with more flexible or bent bridges, such as homophthalate, phenylenedicarboxylate and malonate anions,[13] as summarized schematically in Chart 1.



a. square   b. triangle   c. loop

Chart 1

Interestingly, most of these compounds crystallize in such way that the molecules stack to form channels,[3] which can be filled with other molecules, and the size of the channels can be controlled by the length of the linkers. For example, the $Ru_2(CO)_4L_2$ corner piece produces a molecular square and a molecular loop in conjunction with oxalate and malonate linkers, respectively.[14] Bonar-Law[15] and others[16] before him have shown that bidentate ligands with well-separated carboxylate groups can be used to bind two *cis* equatorial positions of a dimetal unit. For example, with dirhodium units, the use of *m*-$HO_2CC(CH_3)_2O–C_6H_4–OC(CH_3)_2CO_2H$ dicarboxylic acid yields a chelated compound (Chart 2). This chelated species reacts further with rigid dicarboxylic acids to form squares,[15,17] or with pyridine to form π-stacked columns with hexagonal holes.[18] A similar tetracarboxylate has been used to link two dirhodium units into a dimer.[19] With a long rigid dicarboxylate ligand, these dimetal units can be linked together in a vertical manner along the Rh–Rh axis.[20]

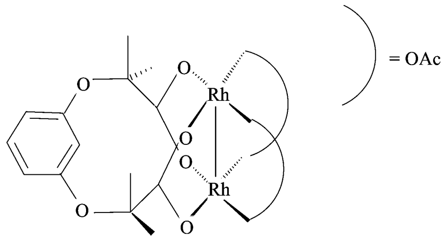


Chart 2

In this report, we describe exploratory work combining quadruply bonded $[Mo_2(DAniF)_2]^{2+}$ units with enantiomerically pure ligands[21,22] of the type shown in Chart 3, which

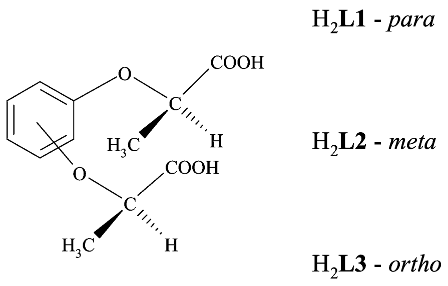


Chart 3

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have been labeled as *p*-H_2**L1**, *m*-H_2**L2** and *o*-H_2**L3** for the *para*-, *meta*- and *ortho*-substituted species, respectively. The *meta* ligand, **L2**$^{2-}$, is akin to the one shown in Chart 2. The latter has Me_2C units, whereas **L2**$^{2-}$ has chiral MeHC units. We report the first structural characterization of a chiral molecular loop and show that it crystallizes to form chiral cavities. We also report the structure of a related dinuclear species in which a dicarboxylate anion wraps around to chelate it.

Results and discussion

The quadruply bonded corner-piece precursor [*cis*-Mo_2(DAniF)$_2$(CH_3CN)$_4$](BF_4)$_2$ (compound **0**) reacts with the tetraethylammonium salt of the chiral dicarboxylate (NEt_4)$_2$**L1** to give [*cis*-Mo_2(DAniF)$_2$]$_2$(**L1**)$_2$ (**1**) in high yield according to eqn. (1).

$$2[\mathit{cis}\text{-}\mathrm{Mo_2(DAniF)_2(CH_3CN)_4}](\mathrm{BF_4})_2 + 2(\mathrm{NEt_4})_2\mathbf{L1} \longrightarrow [\mathit{cis}\text{-}\mathrm{Mo_2(DAniF)_2}]_2(\mathbf{L1})_2 + 4\mathrm{NEt_4BF_4} \quad (1)$$

In this compound, two *cis*-Mo_2(DAniF)$_2$ units are held together by two of the carboxylate anions, producing a molecular loop, as shown in Fig. 1. It is clear that the dicarboxylate anions displace the labile equatorial acetonitrile groups and each of the two **L1** dianions has a carboxylate group attached to each of the two Mo_2^{4+} units, resembling the claws of a crab, as can be seen in Fig. 2. The entire molecule resembles a second-order Möbius strip, which is a Möbius-type ring in which there are two twists (rather than one), both in the same direction. The idealized molecular symmetry would be 222 (D_2 in Schönflies notation). As noted below, the ^{1}H NMR spectrum is consistent with this symmetry.

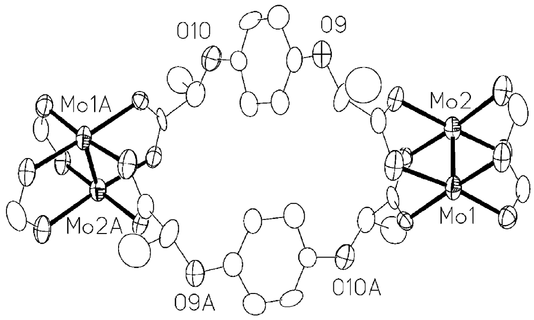


Fig. 1 Thermal ellipsoid plot of **1** with ellipsoids drawn at the 30% probability level. Hydrogen atoms, solvent molecules and anisyl groups have been omitted for clarity.

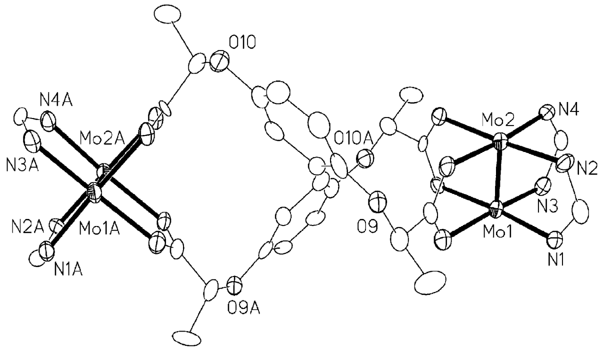


Fig. 2 Thermal ellipsoid plot of **1** showing the twisted nature of the loop. The torsion angle between the two Mo_2 units is 76°. Ellipsoids are drawn at the 30% probability level; hydrogen atoms, solvent molecules and anisyl groups have been omitted for clarity.

Table 1 Selected interatomic distances[a] for **1**·$4CH_2Cl_2$ and **4**·C_6H_6.

	1·$4CH_2Cl_2$	**4**·C_6H_6
Mo–Mo	2.081(2)	2.0812(7)
Mo–N	2.08 [3]	2.112 [2]
Mo–O	2.13 [2]	2.141 [2]
Overall torsion angle[b]	−75.8	—

[a] Distances given in Å. Numbers in square brackets correspond to average values. [b] The torsion angle (in °) is defined as the angle between the two Mo–Mo bonds. Since **4** has only one Mo_2 unit, no torsion angle is given.

Since the two Mo_2 units in each molecule are related by a crystallographic two-fold axis, they are equivalent and the Mo–Mo bond distance of 2.081(2) Å (see Table 1) is similar to those found in other paddlewheel compounds having carboxylate or formamididate bridging ligands.[23] The ligands are attached to each dimolybdenum unit by one carboxyl group, as in other molecular loops, though the conformation here is quite different from those previously described. Loops with the dianions 1,4-phenylenediacetate [*p*-$C_6H_4(CH_2CO_2)_2$], homophthlate [*o*-$C_6H_4(CH_2CO_2)(CO_2)$] and malonate [$CH_2(CO_2)_2$] have the two Mo_2 units essentially parallel to each other.[13] Because of the chiral nature of the ligands in **1**, there is a significant twist between the vectors of the two Mo_2 species, which are at an angle of −75.8°. This twist has consequences in the packing of the molecules (Fig. 3). In the previously described molecular loops,[13] the molecules stack with the Mo–Mo bonds aligned, thus creating channels that can vary in size depending on the length of the linkers. This is not possible in **1** due to the S shape of the molecule. Here again, the molecules stack, but now, parallel stacks of loops form channels along the *a* axis. These channels, which provide a chiral environment because of the chirality of the dicarboxylate linkers, are large enough to allow interstitial solvent molecules to reside in them, as shown in Fig. 3.[24] This could be of importance in enantiomer resolution or in catalysis and efforts are being made to prepare ruthenium and rhodium analogs for which catalytic activity should be highly relevant.[1] In this context, it is important to note that the chiral linker can be made in high purity and very cheaply from readily available commercial sources.[21,22]

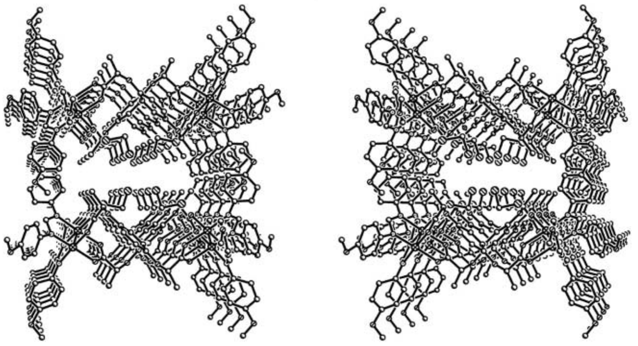


Fig. 3 A stereoscopic view of the packing of **1**·$4CH_2Cl_2$ showing channels filled with dichloromethane guest molecules.

The first stage of the ligand synthesis has been described as taking place *via* a nucleophilic attack, which inverts the *S* conformation of the ethyl lactate triflate derivative to the *R* conformation for the precursor of the linker. Effenberg and coworkers showed by chiral gas chromatography that the reaction occurs with 92% enantiomeric inversion.[22] We also determined the enantiomeric purity of the (NEt_4)$_2$**L1** salt by NMR spectroscopy and found it to be similar, that is, *ca.* 95%. For **1**, the cyclic voltammogram (CV) and differential pulse voltammogram (DPV) show a single reversible oxidation wave at 0.388 V *versus* Ag/AgCl, which is similar to that for [*cis*-Mo_2(DAniF)$_2$]$_2$($O_2CCH_2C_6H_4CH_2CO_2$)$_2$.[13] The NMR spectrum (*vide infra*), electrochemical measurements and elemental analysis indicate that the purity of the product is good.

The ^1H NMR spectrum in acetone-d_6 shows the singlet at 8.55 ppm for the methine proton of the formamidinate ligands and two singlets in a 1 : 1 ratio for the OCH_3 groups of the anisyl groups at 3.68 and 3.70 ppm, which is in agreement with D_2 being the highest possible symmetry of the molecule. A complicated multiplet in the range 6.62 to 6.98 ppm corresponds to the aromatic protons of the anisyl groups and those of the linkers. The remaining signals for the chiral linkers are a quartet at 5.23 ppm for the CH unit and a doublet for CH_3 at 1.74 ppm. The ratio of carboxylate to formamidinate signals of 1 : 2 is consistent with a structure of D_2 symmetry.

Exploration of reactions with analogous ligands

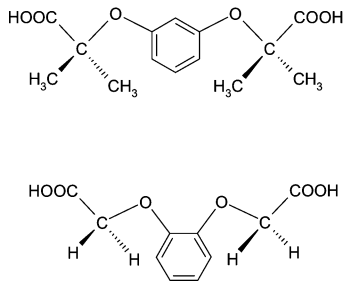
Reactions similar to that in eqn. (1) have been carried out for the isomeric *ortho* and *meta* ligands using the corresponding tetraethylammonium salts $(NEt_4)_2$**L2** and $(NEt_4)_2$**L3**. Because of the smaller bite angles of these ligands it was considered less likely that they could form compounds similar to **1**. Nevertheless, we decided to investigate their reactivity towards the corner-piece precursor **0** to determine how the geometry of the ligands might impact the structure of the dimolybdenum compounds. This is important as small changes in the structures of the ligand can have a significant effect on the structure of the metal complexes and the manner in which they pack in the crystal.[3]

Reactions of **0** and **L2**$^{2-}$ or **L3**$^{2-}$ proceeded similarly to that for the preparation of **1** with the formation of yellow solids, **2** and **3**, in high yields that show δ⟶δ* transitions at 410 and 412 nm, respectively. These are similar to that for **1**, which occurs at 428 nm in CH_2Cl_2 solution. Like that for **1**, the results of the elemental analyses were consistent with the empirical formula $Mo_2C_{42}H_{42}N_4O_{10}$ (*i.e.* 1 : 1 adducts of **L2** or **L3** with an $Mo_2(DAniF)_2$ unit). The ^1H NMR spectrum of **2** in C_6D_6 is similar to that of **1**, indicating the formation of a single product with a formamidinate to carboxylate ratio of 2 : 1. But whether this is a chelated dinuclear compound with C_2 symmetry or a tetranuclear loop like **1** cannot be determined solely by analysis of the ^1H NMR spectrum.

Sharp signals in the ^1H NMR spectrum of **3** in C_6D_6 indicate that the product is diamagnetic, as required by the presence of the quadruply bonded Mo_2 unit. The spectrum is more complex, however, having two singlets at 8.42 and 8.49 ppm in a ratio of *ca.* 1 : 2 that correspond to methine groups. There are also two doublets in a similar ratio at 1.91 and 1.98 ppm for the CH_3 groups at the chiral centers and two quartets assigned to CH groups at the chiral centers at 5.22 and 5.51 ppm. A complicated multiplet in the range 6.50 to 6.64 ppm corresponds to the aromatic protons of the anisyl groups and those of the linkers. This doubling of the signals suggests the formation of two products which are isolated in a relative ratio of 1 : 2. The CV is also consistent with the presence of two species in solution.

Because attempts at crystallizing **2** and **3** produced only amorphous materials unsuitable for single crystal X-ray diffraction, we tried to gain insight by looking at the type of products formed by analogous non-chiral ligands in which the OCMeHCO$_2$ groups are replaced by $OC(Me)_2CO_2$ groups to give the *meta* analog H_2**L4**,[15] or by OCH_2CO_2 groups to give the *ortho* analog H_2**L5**[25] (Chart 4).

Using **L4**$^{2-}$, a reaction with **0** was performed in CH_3CN following eqn. (1). The yellow solid which formed was dissolved in C_6H_6 and this solution was mixed with hexanes to produce crystals of *cis*-$Mo_2(DAniF)_2$(**L4**)·C_6H_6 (**4**·C_6H_6). The ^1H NMR spectrum in C_6D_6 shows the presence of one compound (**4**) with a carboxylate to formamidinate ratio of 1 : 2, as in **2**. A singlet at 8.46 ppm corresponds to the methine protons. We observed only one singlet for the OCH_3 groups at 3.19 ppm and a doublet for the methyl groups of the non-chiral dicarboxylate at 1.96 ppm, which is in agreement with a molecule in an idealized C_{2v} symmetry (*vide infra*). The CV and DPV show a single reversible oxidation wave at 0.344 V *versus* Ag/AgCl. The ^1H NMR spectrum, electrochemical measurements and elemental analysis indicate that the purity of the product is good.



H_2**L4**

H_2**L5**

Chart 4

The structure of **4** (Fig. 4) shows that the dicarboxylate anion wraps around the dimetal unit to form a chelate in the same way as described by others for similar Rh_2^{4+} compounds.[15,16] The Mo–Mo bond distance of 2.0812(7) Å (see Table 1) is similar to that in other paddlewheel compounds having mixed carboxylate and formamididate bridging ligands. Because of the similarity of **L2**$^{2-}$ and **L4**$^{2-}$, it is likely that the structure of **2** is similar to that of **4** and thus **2** has a chelated dicarboxylate anion and only one Mo_2^{4+} unit.

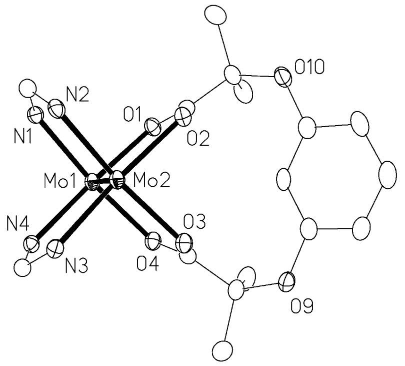


Fig. 4 Thermal ellipsoid plot of **4** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, interstitial solvent molecules and anisyl groups have been omitted for clarity.

A similar reaction of **0** with **L5**$^{2-}$ was performed in CH_3CN and a crystalline product (**5**) was obtained by extracting the product with hot CH_2Cl_2, then adding hexanes and storing at −10 °C. Unfortunately these crystals diffracted poorly and were twinned, which prevented a structural characterization, but the product was analyzed by ^1H NMR spectroscopy. The spectrum in $CDCl_3$ of either the crystals or the yellow powder shows the presence of the carboxylate and formamidinate ligands in a 1:2 ratio but as in the reaction with **L3**$^{2-}$, the signals show signs of doubling suggesting again the presence of two compounds but in a 1:3 ratio. There are two singlets at 8.42 and 8.40 ppm from methine groups (ratio of 1:3), two singlets at 3.64 and 3.67 ppm for two types of OCH_3 groups, and two singlets at 5.18 and 5.22 ppm assigned to the CH_2 groups. A complicated multiplet in the range of 6.47 to 7.10 ppm corresponds to the aromatic protons of the anisyl groups and those of the linkers. This suggests again the formation of two types of products, possibly a loop and a chelated product, analogous to those obtained with **L3**$^{2-}$. The UV-vis spectra for **4** and **5** show δ⟶δ* transitions at 430 and 431 nm, respectively, consistent with the presence of an Mo_2^{4+} core.

Conclusions

We have shown that the type of compound formed between quadruply bonded Mo_2^{4+} units in a *cis*-$Mo_2(DAniF)_2$ species and chiral and non-chiral dicarboxylate anions derived from *ortho*, *meta* and *para* substitution of aromatic entities such as those in **L1**$^{2-}$–**L5**$^{2-}$ is very dependent on the ligand configuration, with those having *para* substitution favoring the formation of molecular loops and those with *meta* substitution favoring dinuclear complexes in which the dicarboxylate gives a chelate. Enantiomerically pure compounds **1** and **2** were obtained. Insight into the structure of **2** was obtained by making a non-chiral analog, namely **4**. The structure of the loop **1** shows channels capable of holding guest molecules. This opens the possibility for using dirhodium instead of dimolybdenum units, which might be useful as catalysts.

Experimental

General

Unless otherwise stated, all operations were carried out in Schlenkware under an inert atmosphere using carefully dried and oxygen-free solvents. Acetonitrile was dried by distillation over CaH_2 in a nitrogen atmosphere. Ethanol was prepared by boiling with $Mg(OEt)_2$ in a nitrogen atmosphere, followed by distillation. All other solvents were purified using a Glass Contour solvent purification system. *cis*-$Mo_2(DAniF)_2(CH_3CN)_4{\cdot}2BF_4{\cdot}2CH_3CN$[26] (**0**), the chiral diacids[21,22] *o*-H_2**L3**, *m*-H_2**L2** and *p*-H_2**L3**, and the non-chiral diacid *m*-$HO_2C(CH_3)_2O–C_6H_4–OC(CH_3)_2CO_2H$, H_2**L4**, were prepared following published methods.[15] The non-chiral *ortho* ligand H_2**L5** was prepared as described below, following a modified experimental procedure.[25] Commercially available chemicals were used as received. IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer from KBr pellets. ^1H NMR spectra were obtained on a Varian XL-300 spectrometer, with chemical shifts (δ/ppm) referenced to the signal of the deuterated solvent. Elemental analyses were performed by Canadian Microanalytical Services in British Columbia, Canada. The electrochemical measurements were recorded on a BAS 100 electrochemical analyzer, with Bu_4NPF_6 (0.1 M) electrolyte, Pt working and auxiliary electrodes, and a Ag/AgCl reference electrode, at a scan rate of 100 mV s^{-1} (for CV). UV-vis measurements were made with a UV2501 PC spectrophotometer.

Preparation of $(Et_4N)_2$L1, $(Et_4N)_2$L2, $(Et_4N)_2$L3 and $(Et_4N)_2$L4. The salts were obtained by adding a 0.1 M solution of Et_4NOH in MeOH (1.15 g, 7.87 mmol) to a 1 M solution of the corresponding H_2L acid in MeOH (1.00 g, 3.94 mmol). After stirring for a few minutes, the solvent was removed under vacuum and the residue was dried under vacuum overnight at 50 °C. For $(Et_4N)_2$**L1**, ^1H NMR ($CDCl_3$, δ): 1.16 (t, NCH_2CH_3, 24H), 1.54 (d, $CHCH_3$, 6H), 3.19 (q, NCH_2CH_3, 16H), 4.53 (q, $CHCH_3$, 2H), 6.61–6.94 (m, aromatic, 4H); for $(Et_4N)_2$**L2**, ^1H NMR ($CDCl_3$, δ): 1.22 (t, NCH_2CH_3, 24H), 1.48 (d, $CHCH_3$, 6H), 3.26 (q, NCH_2CH_3, 16H), 4.52 (q, $CHCH_3$, 2H), 6.33–6.99 (m, aromatic, 4H); for $(Et_4N)_2$**L3**, ^1H NMR (CD_3COCD_3, δ): 1.55 (t, NCH_2CH_3, 24H), 1.64 (d, $CHCH_3$, 6H), 3.68 (q, NCH_2CH_3, 16H), 4.47 (q, $CHCH_3$, 2H), 6.99 (s, aromatic, 4H); for $(Et_4N)_2$**L4**, ^1H NMR ($CDCl_3$, δ): 1.20 (t, NCH_2CH_3, 24H), 1.50 [s, $C(CH_3)_2$, 12H], 3.25 (q, NCH_2CH_3, 16H), 6.47–6.77 (m, aromatic, 4H).

Preparation of $(Et_4N)_2$L5. A solution of $ICH_2CO_2C_2H_5$ (0.936 g, 4.37 mmol) in 10 ml of CH_3CN, which was prepared in a flask protected from light by aluminium foil, was added *via* cannula to a suspension of catechol (0.2372 g, 2.156 mmol) and K_2CO_3 (0.716 g, 5.19 mmol) in 10 ml of CH_3CN. The mixture was stirred overnight in a flask wrapped with aluminium foil. The solvent was then removed under vacuum and the residue was dissolved in 30 ml of CH_2Cl_2; an insoluble portion was removed by filtration. The CH_2Cl_2 was removed from the filtrate and yielded the corresponding diester Et_2**L5**.

Hydrolysis of the diester was performed, as previously described[21,22] for Et_2**L1**, Et_2**L2** and Et_2**L3**, by stirring it for 2 h with NaOH in H_2O–MeOH solution. The insoluble H_2**L5** was collected by filtration and used without further purification. Neutralization with Et_4NOH was performed as described above for the other chiral ligands. ^1H NMR ($CDCl_3$, δ): 1.20 (t, NCH_2CH_3, 24H), 3.30 (q, NCH_2CH_3, 16H), 4.36 (s, CH_2, 4H), 6.68–6.85 (m, aromatic, 4H).

Preparation of $[Mo_2(DAniF)_2(L1)]_2$ (1). A mixture of **0** (0.300 g, 0.267 mmol) and $(NEt_4)_2$**L1** (0.137 g, 0.267 mmol) was placed in one flask. In another flask, 10 ml of CH_3CN was degassed by freezing in liquid nitrogen and pumping under vacuum. The solvent was then added to the solid mixture *via* cannula. A yellow solid formed upon mixing. The mixture was stirred for 30 min, the solvent decanted *via* cannula and the yellow residue was washed with EtOH and hexanes. The yield was essentially quantitative. IR (KBr, cm^{-1}): 3448 (w, br), 2935 (w), 2832 (w), 1609 (w), 1542 (s), 1503 (vs), 1461 (m), 1441 (m), 1415 (w), 1292 (m), 1245 (s), 1217 (s), 1177 (m), 1103 (m), 1035 (s), 941 (w), 874 (w), 827 (m), 764 (w), 703 (w), 644 (w), 619 (w), 591 (w), 522 (w), 453 (w). Elemental analysis, calc. for $Mo_4C_{84}N_8O_{25}H_{94}$: C, 50.46; H, 4.74; N, 5.60; found: C, 50.37; H, 4.47; N, 5.55%. ^1H NMR (CD_3COCD_3, δ): 1.74 (d, $CHCH_3$, 12H), 3.68 (s, OCH_3, 12H), 3.70 (s, OCH_3, 12H), 5.23 (q, $CHCH_3$, 4H), 6.62–6.98 (m, aromatic, 40H), 8.55 (s, CH, 4H). Crystals of **1** were obtained by dissolving the yellow solid in 10 ml of CH_2Cl_2 and layering the solution with 40 ml of hexanes. Needle-like yellow crystals, suitable for X-ray single crystal diffraction, formed within 24 h.

Preparation of $Mo_2(DAniF)_2(L2)$ (2). This was prepared similarly to **1**. The yield was quantitative. IR (KBr, cm^{-1}): 3448 (w, br), 2935 (w), 2832 (w), 1609 (w), 1542 (s), 1503 (vs), 1461 (m), 1441 (m), 1415 (w), 1292 (m), 1245 (s), 1217 (s), 1177 (m), 1103 (m), 1035 (s), 941 (w), 874 (w), 827 (m), 764 (w), 703 (w), 644 (w), 619 (w), 591 (w), 522 (w), 453 (w). Elemental analysis, calc. for $Mo_2C_{42}N_4O_{13}H_{48}$: C, 50.01; H, 4.80; N, 5.55; found: C, 49.87; H, 4.58; N, 5.29%. ^1H NMR (C_6D_6, δ): 1.83 (d, $CHCH_3$, 6H), 3.17 (s, OCH_3, 6H), 3.19 (s, OCH_3, 6H), 5.02 (q, $CHCH_3$, 2H), 6.39–7.26 (m, aromatic, 20H), 8.48 (s, CH, 2H).

Preparation of $Mo_2(DAniF)_2(L4)$ (4). This was prepared similarly to **1**. Yield: (90%). IR (KBr, cm^{-1}): 2986 (w), 2944 (w), 2905 (w), 2831 (w), 1696 (w), 1594 (m), 1534 (s), 1499 (s), 1467 (m) 1439 (w), 1413 (w), 1362 (w), 1312 (m), 1284 (m), 1244 (s), 1210 (m), 1176 (m), 1036 (m), 826 (m), 779 (w), 780 (w), 700 (w), 621 (w), 588 (w), 537 (w), 450 (w). Elemental analysis, calc. for $Mo_2C_{47}N_4O_{10}H_{49}$: C, 55.25; H, 4.83; N, 5.48; found: C, 55.46; H, 4.85; N, 5.09%. ^1H NMR (C_6D_6, δ): 1.96 [s, $C(CH_3)_2$, 12H], 3.19 (s, OCH_3, 12H), 3.19 (s, OCH_3, 6H), 5.02 (q, $CHCH_3$, 2H), 6.39–7.26 (m, aromatic, 20H), 8.48 (s, CH, 2H).

Reaction of 0 with $(NEt_4)_2$L3. This was carried out similarly to the preparation of **1**. IR (KBr, cm^{-1}): 3034 (w), 2933 (w), 3831 (w), 1560 (m), 1542 (s), 1500 (vs), 1459 (m), 1440 (m), 1291 (m), 1411 (m), 1291 (m), 1246 (s), 1214 (s), 1104 (m), 1031 (s), 940 (w), 878 (w), 825 (s), 762 (w), 590 (w), 532 (w), 449 (w). Elemental analysis, calc. for $Mo_4C_{84}N_8O_{25}H_{94}$: C, 50.46; H, 4.74; N, 5.60; found: C, 50.70; H, 4.84; N, 5.91%. ^1H NMR (C_6D_6, δ): 1.91, 1.98 (2d, $CHCH_3$, 18H), 3.11, 3.19 (2d, OCH_3, 36H), 5.22, 5.51 (2q, $CHCH_3$, 6H), 6.36–7.42 (m, aromatic, 60H), 8.42, 8.49 (2s, CH, 6H).

Reaction of 0 with $(NEt_4)_2$L5. A yellow solid was obtained following the procedure for the preparation of **1**. IR (KBr, cm^{-1}): 2947 (w), 2832 (w), 1623 (m), 1543 (s), 1534 (s), 1500 (vs), 1452 (m), 1426 (m), 1384 (w), 1341 (w), 1286 (s), 1246 (s), 1215 (s), 1176 (w), 1131 (w), 1106 (w), 1030 (m), 941 (w), 830 (m), 789 (w), 763 (w), 742 (w), 712 (w), 618 (w), 592 (w), 542 (w), 470 (w), 449 (w). Elemental analysis, calc. for Mo_2C_{40}-

Table 2 Crystal data for **1**·4CH_2Cl_2 and **4**·C_6H_6

	1·4CH_2Cl_2	**4**·C_6H_6
Formula	$Mo_4N_8O_{20}C_{88}Cl_8H_{92}$	$Mo_2N_4O_{10}C_{50}H_{52}$
Formula weight	2249.06	1060.84
Space group	$I222$ (no. 23)	$P2_1/c$ (no. 14)
a/Å	13.970(3)	16.837(5)
b/Å	20.450(5)	16.094(5)
c/Å	37.216(5)	19.036(6)
β/°	90	115.727(5)
V/Å^3	10632(4)	4647(3)
Z	4	4
D_c/g cm^{-3}	1.405	1.516
μ(Mo-Kα)/mm^{-1}	0.726	0.604
T/°C	−60	−173
$R1$[a], $wR2$[b] [$I > 2\sigma(I)$]	0.1102, 0.2226	0.0334, 0.0746
$R1$[a], $wR2$[b] (all data)	0.1488, 0.2404	0.0457, 0.0796
Flack parameter[c]	0.03(14)	

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$. [c] See: H. D. Flack, *Acta Crystallogr. Sect. A*, 1983, **39**, 876.

$N_4O_{11}H_{40}$: C, 50.86; H, 4.27; N, 5.78; found C, 50.77; H, 4.10; N, 5.57%. ^{1}H NMR ($CDCl_3$, δ): 3.64, 3.68 (2s, OCH_3, 36H), 5.18, 5.22 (2s, CH_2, 12H), 6.44–7.10 (m, aromatic, 60H), 8.39, 8.42 (2s, CH, 6H)

X-Ray crystallography

For **1**, a single crystal was mounted on the tip of a quartz fiber and transferred to the goniometer of an Enraf-Nonius FAST diffractometer. 250 strong reflections were indexed to a body-centered orthorhombic unit cell. The cell dimensions, lattice type and Laue symmetry were confirmed from axial images. Data collection and integration were performed using the MADNES software[27] and the integrated data were processed and corrected for Lorentz and polarization effects with the program PROCOR.[28] An absorption correction was applied using the program SORTAV.[29] The crystal showed broad reflections in ω indicative of a high degree of mosaicity. A single crystal of **4** was mounted on a nylon loop and transferred to the goniometer of a SMART APEX CCD diffractometer. Data collection and integration were performed with the SMART software[30] and the integrated data were processed and corrected for Lorentz and polarization effects using the SAINT program.[31] An absorption correction was applied with the program SADABS.[32] Both structures were solved by the Patterson method and refined by alternate cycles of full-matrix least squares and difference Fourier maps with the SHELXTL package.[33] Except for the disordered aryl groups found in **1** and O6A in **4**, non-hydrogen atoms were refined anisotropically and hydrogen atoms were added at calculated positions and included in the structure factor calculations. Selected bond distances for **1** and **4** are listed in Table 1. Crystal data are listed in Table 2.

CCDC reference numbers 217277 and 217278.

See http://www.rsc.org/suppdata/dt/b3/b310151g/ for crystallographic data in CIF or other electronic format.

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