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Discrete and polymeric ensembles based on dinuclear molybdenum(vi) building blocks with adaptive carbohydrazide ligands: from the design to catalytic epoxidation

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Symmetrical disubstituted carbohydrazides (H_4L^{1-6}) when reacted with [$MOO_2(acac)_2$] (in 1:2 molar ratio) afford the corresponding discrete complexes, [$(MOO_2)_2L^{1.5.6}(MeOH)_2$], [$(MOO_2)_2L^{1.5.6}(Im)_2$] (Im = imidazole), and/or polymeric ensembles, [$(MOO_2)_2L^{1-6}$]_n, depending on the reaction solvent, the ligand framework and the presence of ancillary coordinating species. In these assemblies, asymmetrical dimolybdenum(v1) entities, [$(MOO_2)_2L^{1-6}$], wherein the corresponding carbohydrazide acts as an adaptable two-compartment ligand offering *ONO* and *ONN* coordination environments, serve as the main building blocks. The solid-state structures of the obtained materials were elucidated *via* X-ray diffraction and infrared spectroscopy, whereas the behaviour of polymeric ensembles in DMSO-*d*₆ solution was investigated by nuclear magnetic resonance. Thermal studies unveiled that the discrete species transfer to the corresponding polymeric ensembles upon heating, whereas upon grinding they either remain intact or afford their reactive and coordinatively unsaturated (pentacoordinated) counterparts. While the discrete methanol-based complexes have a comparable spatial arrangement of ancillary ligands, imidazole-based ones offer substantially different scenario which was addressed in detail *via* density functional theory calculations. Finally, the polymeric ensembles were shown to be efficient catalysts for cyclooctene epoxidation under eco-friendly conditions while employing aqueous *tert*-butyl hydroperoxide as an oxidant.

Introduction

The development of di- or trinuclear metal-organic complexes, which can be rearranged so to serve as building blocks (tectons) for larger architectures, is one of the thriving areas of the modern inorganic chemistry.¹ Preferably, such complexes have only the specific coordination sites labile and thus prone to the ligand exchange, while the remaining sites should be inert. Archetypical examples of this class of complexes include carboxylate paddlewheel species,² as well as homo- and heterodinuclear complexes with macrocyclic compartmental

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ligands.³ While these entities have their own merits, as *e.g.* catalytic or magnetic systems,⁴ their inclusion into larger assemblies can deliver materials with novel functionalities. Naturally, ensembles based on this kind of- building blocks have been well recognized in numerous fields of chemistry and physics, including catalysis,⁵ magnetism,⁶ and gas storage⁷.

One of the routes towards *e.g.* dinuclear entities that can act as tectons takes advantage of the cations or the oxo-species with well-defined coordination preferences and multitopic ligands having a suitable spatial arrangement of the chelating compartments.^{3,8} While macrocyclic ligands of the salen-type have been regularly used for such purposes, especially for the design of catalytically active systems,⁹ recent studies have unveiled the vast potential of flexible multi-compartment hydrazones in this context.¹⁰ Among them, carbohydrazides are particularly appealing as their conformational and tautomeric adaptability allows the formation of dinuclear entities, which can aggregate further into tetra- or octanuclear ensembles.¹¹

Among a variety of metal complexes that have been investigated as catalysts for the epoxidation of olefins,¹² those of molybdenum have been especially well recognized.¹³ For instance, mononuclear Mo(vI) complexes with *ONO* hydrazones have been extensively studied as catalysts for the epoxidation of cyclooctene under eco-friendly organic-solvent-free conditions, using *tert*-butyl hydroperoxide (TBHP) as an oxidant.^{14,15} The activity of such complexes is largely related to their structures, where Mo(vI) cation usually has one labile

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Electronic Supplementary Information (ESI) available, containing crystallographic data, spectroscopy data, thermograms, PXRD patterns, theoretical calculation data and catalysis data, organized according to the manuscript. CCDC 1983030-1983037
 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. See DOI: 10.1039/x0xx0000x

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dinuclear and polymeric DOI: 10.1039/D0NJ01045F Scheme 1. Synthetic routes to discrete molybdenum(vi) complexes R₃ R3 (i) (ii) [(MoO₂)₂(L)(CH₃OH)₂] [(MoO₂)₂(L)]_n [(MoO₂)₂(L)(Im)₂] (1a, 5a, 5a', 6a) (1-6) (1b, 5b, 6b) 📥 = CH₃OH 📩 = Im (R3) O Mo D≡ o^oMo 0-Mo $\mathbf{H_4L^1, R_1} = R_2 = R_3 = H$ H_4L^4 , $R_1 = R_3 = H$, $R_2 = -OH$ H_4L^2 , $R_1 = R_2 = H$, $R_3 = -C_4H_4$ H_4L^5 , $R_1 = -OCH_3$, $R_2 = H$, $R_3 = H$ H_4L^3 , $R_1 = -OH R_2 = H$, $R_3 = H$ H_4L^6 , $R_1 = R_3 = H$, $R_2 = -OCH_3$ (i) $H_4L^1-H_4L^6$, CH_3CN , ≈ 65 °C; (ii) H_4L^1 , H_4L^5 , H_4L^6 , CH_3OH , ≈ 65 °C; (iii) H_4L^1 , H_4L^5 , H_4L^6 , CH_3OH , ≈ 65 °C; (iii) H_4L^1 , H_4L^5 , H_4L^6 , CH_3OH , ≈ 65 °C; (iii) H_4L^1 , H_4L^5 , H_4L^6 , H_4L^6 , H_4C^6 , H_4C^6, H_4C^6 , H_4C^6 , H_4C^6 , H_4C^6

was also the case here, thus allowing for the formation of $[(MoO_2)_2(L^{1-6})]_n$ (1–6).

When conducted in methanol (good donor solvent), reactions of H_4L^1 , H_4L^5 or H_4L^6 and $[MoO_2(acac)_2]$ in the molar ratio 1:2 yielded the corresponding dinuclear complexes of the composition [(MoO₂)₂(L^{1,5,6})(MeOH)₂], namely, **1a**, **5a·CH₃OH**, 5a'.0.64CH₃OH and 6a (Scheme 1, route (ii)), occasionally together with negligible amounts of the corresponding polymers 1, 5 and 6. The remaining ligands under the same conditions gave exclusively polymeric products, 2, 3 and 4, identical to those obtained from acetonitrile. In order to find a more efficient route to pure 1a, 5a·CH₃OH, 5a'·0.64CH₃OH and 6a, we explored the influence of an additive on the crystallisation outcome. Crystallisation can be, in certain cases, controlled via soluble or insoluble additives.²³ This approach is typically employed for crystallisation of proteins, but nowadays it is increasingly recognized by the pharmaceutical industry in the context of polymorph resolution and crystal morphology control.^{23f)} In previous studies, we have demonstrated the significance of 4,4'-bipyridine (4,4'-bipy) as an additive for successful polymorph resolution, ^{21e)} whereas here we aimed to test its ability to (sterically) hamper polymerisation. Indeed, an introduction of 4,4'-bipy in sub-stoichiometric amounts (managing in this way competition for coordination to Mo centres) into reaction mixtures proved to be a very fruitful approach to pure 1a, 5a·CH₃OH, 5a'·0.64CH₃OH and 6a. It should be noted that such an approach also improved the yields of the corresponding compounds. However, the same tactic was not as successful in the case of reactions with H_4L^2 , H_4L^3 and H_4L^4 ligands, where exclusively polymers $[(MoO_2)_2(L^{2,3,4})]_n$ were formed. Moreover, it is important to highlight that complex $[(MoO_2)_2(L^5)(MeOH)_2]$ yielded two solvates in the solid state,

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coordination site, and can under proper conditions switch between penta- and hexacoordinated forms. The possibility to tune the catalytic activity of analogous complexes by slightly altering the ligand structure naturally opens new paths in their design.¹⁶ One of such, inspired by the prospects of the cooperative catalysts,¹⁷ addresses the development of di- or trinuclear Mo(vi) complexes with multi-compartment hydrazones whose binding pockets structurally replicate those of the mononuclear complexes.¹⁸ Since the corresponding complexes can show higher catalytic activity then the mononuclear ones, or the ability to catalyse the different group of reactions, the development of the field, as illustrated by examples of V and Ni dinuclear complexes based on comparable ligands, comes as no surprise.^{19,20}

In light of previous considerations we aimed to explore both structural and catalytic opportunities of dinuclear Mo(vi) complexes based on adaptable hydrazone frameworks,¹¹ⁱ in which the molybdenum centres assume different coordination environments. As ligands capable of imposing asymmetrical coordination we chose carbohydrazides.²⁰ Namely, herein we report a comprehensive solid-state and solution study of discrete and polymeric ensembles based on asymmetrical dinuclear Mo(vi) building blocks, comprising adaptive carbohydrazide ligands with ONO and ONN chelating compartments. Isolated materials were investigated in the solid state via X-ray diffraction, infrared (IR) spectroscopy and thermogravimetric analysis (TGA), whereas their structures in solution were elucidated by nuclear magnetic resonance (NMR). Moreover, stability and (inter)conversions between discrete dinuclear and polymeric ensembles were closely examined via mechanochemical and thermal studies and additionally addressed by "soaking" experiments. Finally, polymeric ensembles were tested as catalysts for cyclooctene epoxidation under organic solvent-free conditions, respecting the rules of green chemistry.

Results and Discussion

Synthetic considerations

Reactions of the symmetric carbohydrazide based ligands $(H_4L^1-H_4L^6)$ with $[MoO_2(acac)_2]$ in the molar ratio 1:2, in acetonitrile, gave complexes of the composition $[(MoO_2)_2(L^{1-6})]$ (Scheme 1, route (i)). Although the solid-state structure of the isolated materials has not been explicitly determined by X-ray diffraction, evaluation and comparison of the relevant spectroscopic data (vide infra) with their mononuclear counterparts firmly suggests the polymeric nature of the compounds.²¹ Indeed, it is well documented that mononuclear dioxomolybdenum(vi) complexes with tridentate ligands, in the absence of a suitable ancillary donor (e.g. a solvent molecule or a functional group of the ligand able to complete the octahedral coordination around the metal), will polymerize via Mo=O···Mo interactions and rarely remain under the pentacoordinated form. Such a scenario is often observed when the reaction is conducted in a poor donor solvent, like acetonitrile,^{21,22} which

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5a·CH₃OH and **5a'·0.64CH₃OH**, with former converting to the latter upon exposure to ambient conditions.

The reactions of H_4L^1 , H_4L^5 or H_4L^6 with $[MoO_2(acac)_2]$ in acetonitrile with the addition of a stoichiometric amount of imidazole gave complexes $[(MoO_2)_2(L^{1,5,6})(Im)_2]$, *i.e.* **1b·CH₃CN**, **5b·CH₃CN** and **6b·2CH₃CN**, respectively. A similar trend in a tendency for polymerisation, as established for the reactions in methanol, was observed here as well. Namely, the H_4L^2 , H_4L^3 and H_4L^4 ligands under stated conditions yielded again only polymeric complexes **2**, **3** and **4**, respectively.

Molecular and crystal structures

Molecular and crystal structures of the H_4L^6 ligand and dinuclear complexes (1a, 1b·CH₃CN, 5a·CH₃OH, 5a'·0.64CH₃OH, 5b·CH₃CN, 6a and 6b·2CH₃CN) described here were determined *via* single-crystal X-ray diffraction (SC-XRD) experiments. Summary of the relevant crystal data for the compounds is given in the Table S1. The description of the molecular and crystal structure of the H_4L^6 ligand given in the ESI (Figures S1-S2, Tables S2-S3).

In all examined discrete dinuclear complexes, ligands are coordinated as tetraanions in the same tautomeric form, enolimino one, both considering the aldehyde residues and the central carbamide fragment (Scheme 1; ESI, Scheme S1/form III, Figure S3, Tables S4-S6). Moreover, the ligand in all cases assumes an *anti*-conformation, creating two coordinating compartments, one with the *ONO* and one with the *ONN* donor atoms (ESI, Figure S3). One [MOO₂]²⁺ unit is anchored in each compartment, *via* O1, N1, O2 (and O10, N5, O11 for **1a**) and N2, N4, O3 (and N6, N8, O12 for **1a**) atoms. Finally, the coordination sphere of each Mo atom is fulfilled by an appropriate auxiliary ligand, *i.e.* the oxygen atom of the methanol molecule (in **1a**, **5a**, **5a'** and **6a**, as in Figure 1) or the nitrogen atom of the imidazole molecule (in **1b**, **5b** and **6b**). At this point, it is



Figure 1. (a) Molecular structure of complex 1a, as an illustrative example of the methanol-based complexes. For clarity, only one molecule of the asymmetric unit is shown. The displacement ellipsoids are drawn at 50% probability level at 296 K. Hydrogen atoms are presented as spheres of arbitrary small radii. (b) Overlay of the two molecules found in the asymmetric unit of 1a.



Figure 2. Supramolecular arrangements: (a) dimers; and (b) chains, found in the crystal structure of **1a**. Hydrogen bonds of the O–H···N and O–H···O type are presented by orange dashed lines, while C–H···O interactions are highlighted as black dashed lines. Supramolecular assembly *via* O17–H17O···N7 ($R_2^{\prime}(12)$ motif) and O18–H18O···O14 ($R_2^{\prime}(14)$ motif) hydrogen bonds, whereas the chains rely on O8–H8···N3 ($R_2^{\prime}(12)$ motif) and O9–H9···O7 ($R_2^{\prime}(8)$ motif) hydrogen bonds.

interesting to observe that neutral (non-coordinated) carbohydrazide ligands in the solid state typically assume a synconformation, whereas coordinated ones are found, as mentioned, in the anti-conformation. Moreover, when considering published structures, there seems to be a solid correlation between tautomeric form of the carbamide fragment and the conformation of the carbohydrazide in the solid state. Most of the carbohydrazides in their noncoordinated form are keto-amino tautomers, with respect to the central carbamide part, which assumes a syn-conformation, with exceptions being carbohydrazides lacking groups with hydrogen bonding capabilities on aromatic rings.²⁴ In contrast, most of the enol-imino tautomers, again while considering the carbamide part, in the anionic forms, assume an anticonformation, as observed in the corresponding metal complexes.²⁵

When comparing molecular structures of complexes **1a**, **5a**, **5a'** and **6a**, one can observe significant differences in the ligand planarity and in the mutual orientation of the coordinated methanol molecules (ESI, Figure S5). The latter subsequently dictates supramolecular hydrogen-bonding motifs in the solid state (ESI, Table S7). The illustration of different supramolecular scenarios can be seen with the crystal structure of **1a**, where the asymmetric unit contains two crystallographically independent molecules differing in the relative orientation of the coordinated methanol molecules (Figure 2, ESI, Figure S6). In one complex coordinated MeOH molecules have nearly the

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Figure 3. (a) Molecular structure of complex 1b-CH₃CN, as an illustrative example of the imidazole-based complexes. For clarity, only one molecule of the asymmetric unit is shown. The displacement ellipsoids are drawn at 50% probability level at 150 K. Hydrogen atoms are presented as spheres of arbitrary small radii. (b) Overlapping diagram of the molecular structures for: 1b (dark gray), 5b (purple), and 6b (yellow).

same orientation, whereas in the other they are oriented almost in the opposite direction. In the former case, this leads to the formation of supramolecular dimers via $R_2^2(12)$, and $R_2^2(14)$ motifs, based on O–H···N and O–H···O hydrogen bonds, respectively (ESI, Table S7, Figure S6).²⁶ When the coordinated MeOH molecules assume more or less opposite directions, it leads to the formation of supramolecular chains based on $C_2^2(12)$ motif that can be decomposed into $R_2^2(8)$ and $R_2^2(12)$ motifs, relying on O–H···O and O–H···N hydrogen bonds, respectively (ESI, Table S7, Figure S6).²⁶ Supramolecular assemblies formed in such a way are stabilized and further interconnected by C–H···O interactions.

In the crystal structures of complexes 5a·CH₃OH (ESI, Figure S7) and 6a (ESI, Figure S8) the main motifs are supramolecular dimers, achieved via hydrogen bonding of the coordinated methanol molecules. As in the case of 1a, the dimers are established upon $R_2^2(12)$ and $R_2^2(14)$ graph-set motifs, involving O-H…N and O-H…O hydrogen bonds, respectively (ESI, Table S7).²⁶ Additionally, in the crystal structure of 5a·CH₃OH, methanol molecules are anchored via O-H…O hydrogen bonds and are situated in the voids between the dimers (ESI, Figure S7, Figure S7). In 5a·CH₃OH, as well as in 6a, the supramolecular dimers associate via numerous C-H···O interactions into three-dimensional crystal architectures (ESI, Table S7, Figures S7–S8). In 5a'·0.64CH₃OH (ESI, Figure S9) methanol molecule coordinated to Mo2 atom is disordered over two positions, which reflects also on the disorder of the terminal oxygen atoms (O6A and O6B, as well as O7A and O7B). The disordered methanol molecule in the major position has a similar orientation as the one coordinated to Mo1 atom,



Figure 4. Supramolecular chains observed in the crystal structure of **1b·CH₃CN**. Acetonitrile molecules are omitted for clarity. The N–H···N and O–H···N hydrogen bonds are presented as orange dashed lines, while C–H···O interactions are denoted with black dashed lines. Supramolecular chains form through N8–H8N···N3 ($R_2^2(14)$ motif) and N6–H6N···O4 ($C_1^1(6)$ motif) hydrogen bonds.

whereas the minor component achieves almost the opposite direction. The former situation obviously allows the formation of supramolecular dimers, displaying again $R_2^2(12)$ and $R_2^2(14)$ motifs based on the O–H···N and O–H···O hydrogen bonds,²⁶ while the latter scenario could lead to the formation of supramolecular chains, as observed in **1a**. However, the presence of (disordered) solvent methanol molecules in the crystal structure apparently disturbs the formation of chains.

All three imidazole-based complexes described in this work, 1b·CH₃CN, 5b·CH₃CN and 6b·2CH₃CN, crystallize as solvates (Figure 3, ESI, Figure S10-S13). When referring to their molecular structures, it should be noted that unlike in methanol-based complexes (1a, 5a, 5a' and 6a) where the methanol molecules are in each case situated on the same side of the ligands' plane, this is not the case in the 1b, 5b and 6b complexes. When considering the plane of the ligand, the coordinating imidazole molecules are located on opposite sides in 1b and 5b and on the same side in 6b (Figure 3). Naturally, it leads to different supramolecular architectures in the solid state. Molecular structure of 1b allows the formation of hydrogen-bonded supramolecular chains (Figure 4), which are formed via N–H···N and N–H···O hydrogen bonds having $R_2^2(14)$ and $C_1^1(6)$ graph-set motifs, respectively (ESI, Table S7, Figure S10).^{26a)-c),27} Assemblies formed in this way are stabilized and mutually joined via C-H···O interactions, anchoring at the same time acetonitrile (solvent) molecules present in the voids.

In the structure of **5b·CH₃CN**, imidazole molecule coordinated to Mo1 atom is disordered over two positions, with occupancies \approx 72% for the major, and \approx 28% for the minor component. This situation can be interpreted in terms of two types of

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supramolecular chains (ESI, Figure S11), their formation depending on the relative position of hydrogen-bonding donor and acceptor functionalities. The assembled chains are stabilized and/or connected by C-H--O interactions in the crystal structure, while the acetonitrile molecules are located in the spaces between the chains (ESI, Table S7, Figures S11–S12). As mentioned previously, since the molecular structure of 6b differs from 1b and 5b, in the relative position of the coordinated imidazole molecules it leads naturally to different chain connectivity in terms of graph-set motifs (ESI, Table S7, Figure S13). Here, along with the $C_1^1(6)$ motif involving N–H…O hydrogen bonds and observed in all three structures (1b·CH₃CN, **5b·CH₃CN** and **6b·2CH₃CN**), ^{26a)-c),27} one finds $R_2^2(16)$ type of motif based on N–H…N hydrogen bonds, instead of $R_2^2(14)$ one observed in 1b-CH₃CN and for the major component in 5b·CH₃CN (ESI, Table S7).

Spectroscopic characterisation

IR spectra of the polymeric compounds 1-6 (ESI, Figure S14) are characterized by the presence of broad bands, corresponding to Mo=O···Mo stretching, in the region 770-810 cm⁻¹.^{14a),21} In contrast, methanol-based dinuclear complexes (ESI, Figure S15-S17) unveil symmetric and asymmetric stretching bands of the ${MoO_2}^{2+}$ unit at $\approx 925 \text{ cm}^{-1}$ and $\approx 890 \text{ cm}^{-1}$ respectively. ^{14a),21} Interestingly, in the spectra of imidazole-based complexes, these bands are well separated for the two $\{MoO_2\}^{2+}$ units found in a chemically different environment and appear as four distinct bands in a range of \approx 930 to \approx 880 cm⁻¹. Compounds **1a**, 5a'-0.64CH₃OH, 5a-CH₃OH and 6a additionally display a medium strong band at 1000-1020 cm⁻¹, which corresponds to methanol C-O stretching, and those at 3200-3400 cm⁻¹ belonging to O-H stretching of coordinated and noncoordinated methanol molecules.^{21e)} The bands distinctive for C=O stretching, *i.e.* amide I bands at 1670–1690 cm⁻¹,²⁸ observed for the ligands are not present in the spectra of complexes, thus suggesting coordination of the ligands in the enolate form, while considering their carbamide fragments. Bands associated with the stretching vibrations of the C=N and C=C functionalities, appearing at \approx 1590 cm⁻¹ and \approx 1550 cm⁻¹, respectively, are shifted for about 20 cm⁻¹ to lower wavenumbers as compared to the ligands.²⁸ Finally, it should be noted that IR spectra of complexes 1a and 1b·CH₃CN, as well as 5a·CH₃OH/5a'·0.64CH₃OH and 5b·CH₃CN are fairly similar, thus suggesting comparable molecular structures of those complexes. On the other hand, IR spectrum of 6b·2CH3CN shows significant deviations from that of 6a, which is also supported by X-ray structural analysis and DFT calculation.

NMR spectra of **1–6** were collected in DMSO- d_6 (ESI, Table S8 with numbering according to Figure S18; Figure S19 and S20). Due to donor capacities of the solvent, polymeric nature of the starting complexes is disrupted, and instead the dinuclear complexes $[(MOO_2)_2(L^{1-6})(DMSO)_2]$ are observed. The corresponding NMR spectra do not display the hydrazinic =N– NH and OH(2) signals, which appear in the spectra of the free ligands in the low field region, indicating quadruple deprotonation of the coordinating ligands.²⁸ Both ¹H and ¹³C

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NMR spectra of **1–6** in DMSO- d_6 showed two sets, of signals arising from ONO and ONN coordination 1030/Digated 04to molybdenum atom. The most significant difference between inequivalent signals was noticed for imine carbons 7 and 9, up to 7 ppm. The two sets of aromatic signals experienced deshielding effects, with less pronounced difference between signals of two binding pockets.

The coordination-induced chemical shifts due to deprotonation and enolisation were the most pronounced for C=O carbons which caused deshielding effects of 14.1 (1), 19.4 (2), 19.2 (3), 18.3 (4), 18.8 (5) and 18.1 ppm (6). The other interacting sites, at position 2 (11) and 7 (9) were shifted to a smaller extent (about 5 ppm).

Stability study of complexes

Thermal behaviour of the complexes was studied in the temperature region from 25 to 600 °C, under an oxygen atmosphere (ESI, Figure S21-S33). Apart from 1, which decomposed in one step, the remaining complexes displayed complicated multistep decomposition in the temperature range from \approx 220 °C to \approx 560 °C, with MoO₃ forming as the final product. In the case of methanol-based complexes, 1a, 5a·CH₃OH, 5a'·0.64CH₃OH and 6a, desolvation occurred in the temperature range from \approx 140 °C to \approx 180 °C, counting both for coordinated and non-coordinated solvent, while leaving in all cases corresponding polymeric complexes as the residues (ESI, Figure S34–S36). For imidazole-based complexes, the initial weight losses were coupled with the loss of the acetonitrile molecules entrapped in the crystal, whereas the second step was associated with the degradation of imidazole ligands. The latter process proceeded for 1b·CH₃CN and 5b·CH₃CN at temperatures for about 40 °C higher than for 6b·2CH₃CN, for

Scheme 2. Overview of the (inter)conversion conditions for polymeric and discrete complexes.



While **2**, **3** and **4** do not form stable discrete complexes, **1** and **6** can be derived from their discrete complex counterparts. **5** and its discrete complex **5a** '0.64CH₃OH can be reversibly interconverted by the action of appropriate solvent or solvent mixture. Moreover, **1** and **6** can be reversibly interconverted to their pentacoordinated species, **1**^{*} and **6**^{*}, respectively.

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which it began at about 200 °C. Such behaviour can be associated with the structural differences established for the complexes.

As expected, the polymeric [(MoO₂)₂(L¹⁻⁶)]_n complexes displayed the highest thermal stability, up to at least 300 °C.

Prepared complexes unveiled interesting differences in their solid-state stability (Scheme 2). To assess it in detail, a set of experiments was conducted where both discrete complexes and polymeric species were exposed to solvents, namely methanol, acetonitrile and mixtures thereof. Methanol and acetonitrile were chosen because they were used for the synthesis and the complexes were poorly soluble in both solvents, as well. Polymeric complexes 1, 2, 3, 4 and 6 showed no reaction with the solvents, rendering them as the most stable assemblies under the investigated conditions. In contrast, when 5 was suspended in methanol, one of its two detected solvates, *i.e.* **5a'·0.64CH₃OH** was readily obtained. Such behaviour might be associated with the structural nature of 5, which has, judging by its PXRD pattern, substantially less ordered solid-state structure than 1 and 6. Exposure of 1a, 6a and 5a'.0.64CH₃OH to acetonitrile, or mixtures of acetonitrile with less than 5% methanol v/v (ESI, Figure S37) led to the formation of the corresponding polymers, 1, 6 and 5. Finally, it should be noted that compounds 2, 3 and 4 did not afford stable discrete complexes under any of the investigated conditions.

It is important to highlight that complexes 1a and 6a lose the coordinated methanol via grinding. Such procedure does not yield polymeric ensembles, as indicated by the corresponding IR spectra and PXRD data (Figure 5, ESI, Figure S34 and S38; S36 and S40), but as we anticipate, coordinatively unsaturated discrete complexes, 1* and 6*, wherein the Mo centres assume a pentacoordinated environment. Namely, in comparison with the spectra of 1a and 6a, those of 1* and 6*, do not hold bands characteristic for C–O stretching, which appear at $\approx 1020\ \text{cm}^{-1}$ in the spectra of 1a and 6a (Figure 5; ESI, Figure S38 and Figure S40). Furthermore, when compared with the IR spectrum of 1 and ${\bf 6},$ those of ${\bf 1^*}$ and ${\bf 6^*}$ do not contain bands due to Mo=O···Mo stretching (Figure 5; ESI, Figure S38 and Figure S40), corroborating altogether coordinatively unsaturated nature of 1* and 6*. A similar scenario is known to occur, albeit not that often, for mononuclear *cis*-dioxomolybdenum(vi) complexes based on tridentate ligands, which was already discussed to some extent.²¹ Although the monomeric units in the absence of a suitable donor will most often polymerise via Mo=O···Mo interactions, under certain conditions, e.g. upon grinding, coordinatively unsaturated (pentacoordinated) species can be afforded as well. As such, these systems are highly reactive and will tend to fulfil their coordination spheres either by polymerisation or by attachment of a suitable donor, e.g. solvent molecule(s).^{20d)} Indeed, the exposure of 1* and 6*, obtained by grinding, to methanol offers a reverse scenario, yielding again 1a and 6a, respectively. On the other hand, 1 and 6 are obtained if 1* and 6* are heated, respectively. In contrast to 1a and 6a, 5a·CH₃OH and 5a'·0.64CH₃OH (ESI, Figure S35 and S39) are indifferent even to prolonged grinding.

Theoretical calculations



Figure 5. A significant part of the ATR-FTIR spectra of 1 (black), 1a (red) and 1* (orange). Peaks relevant to the discussion are marked with asterisk (*).

As it was established by X-ray diffraction, complexes **1b** and **5b** accommodate the coordinated imidazole molecules in *trans* arrangement, whereas in **6b** they are found in *cis* position. This unusual behaviour was explored from a theoretical point of view, considering and comparing the relative stability of the relevant *cis* and *trans* species. Moreover, the DFT calculations were performed on a molecular scale to understand weather the stability trend can account for different spatial arrangements observed within the crystal structures.

Since the crystallisation process advances on the starting "seed" structure, it was relevant to consider and limit the calculations at the molecular scale. Accordingly, the cis- and trans- $[(MoO_2)_2(L^i)(Im)_2]$ (i = 1, 5, 6) units were chosen as the potential elementary unit "seeds" whereupon the corresponding crystals form. From a synthetic point of view, it can be considered that such units form via coordination of two imidazole molecules on their "free" parents, *i.e.* the *cis*- and *trans*- $[(MoO_2)_2(L^i)]$ (i = 1, 5, 6), where cis and trans refer to relative position of vacant sites, with both Mo coordination centres being pentacoordinated. Namely, calculations took into account the energy of optimized structures of the "parent" building blocks, *i.e. cis*- and *trans*-[(MoO_2)₂(L^i)] (i = 1, 5, 6), and the potential *cis*and trans- structures having one imidazole coordinated on the most stable coordination site, i.e. the ONO one $[(MoO_2)_2(L^i)(Im^{ONO})]$ (i = 1, 5, 6). All those potential structures have been calculated in the gas phase (where no solvent perturbation is observed) and using the PCM method to mimic the acetonitrile solvent environment. The relative energies have been summarized in Table 1. All energies have been indicated relative to the energy of cis-[(MoO₂)₂(Lⁱ)].

When considering the $[(MoO_2)_2(L^i)(Im)_2]$ structures in the gas phase, the *trans*- $[(MoO_2)_2(L^i)(Im)_2]$ structures turned out to be energetically more favourable than the *cis*- $[(MoO_2)_2(L^i)(Im)_2]$

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Table 1. Relative free energies and energy differences $\Delta E_{cis-trans}$ (in kcal mol⁻¹).of the different species.

E (kcal/mol)	i = 1		i = 5		i = 6	
	Gas	PCM	Gas	PCM	Gas	PCM
cis-[(MoO ₂) ₂ (L ⁱ)]	0.0	0.0	0.0	0.0	0.0	0.0
trans-[(MoO ₂) ₂ (L ⁱ)]	-0.1	+0.8	-0.1	0.2	+1.5	+1.3
$\Delta E_{cis-trans}$	+0.1	-0.8	+0.1	-0.2	-1.5	-1.3
<i>cis</i> -[(MoO ₂) ₂ (L ⁱ)(Im ^{ONO})]	-17.7	-14.7	-17.1	-14.2	-16.8	-14.1
trans-[(MoO ₂) ₂ (L ⁱ)(Im ^{ONO})]	-17.2	-13.7	-16.7	-13.6	-14.7	-12.3
$\Delta E_{cis-trans}$	-0.5	-1.0	-0.4	-0.6	-2.1	-1.8
<i>cis</i> -[(MoO ₂) ₂ (L ⁱ)(Im) ₂]	-28.8	-23.8	-28.0	-23.7	-27.4	-22.7
trans-[(MoO ₂) ₂ (L ⁱ)(Im) ₂]	-31.8	-23.8	-31.1	-23.1	-28.7	-21.3
$\Delta E_{cis-trans}$	+3.0	0.0	+3.1	-0.6	+1.3	-1.4

ones in all cases, with E_{cis} - E_{trans} ($\Delta E_{cis-trans}$) being +3 kcal/mol for L¹ and L⁵ and +1.3 kcal/mol for L⁶ ligands. This preference for the trans structures seems logical due to the nature of the imidazole, being substantially bigger than methanol, where cis- $[(MoO_2)_2(L^{1,5,6})(MeOH)_2]$ structures were observed in all cases. While the established values for $[(MoO_2)_2(L^{1,5})(Im)_2]$ clearly indicate a preference for the trans arrangement, the situation is somewhat ambiguous for [(MoO₂)₂(L⁶)(Im)₂]. Thus, including the correction factor using PCM correction seemed to be important.

The results of such calculations unveil negligible differences between the *cis* and *trans* structures in case of L^1 ($\Delta E_{cis-trans} =$ 0.0) and L⁵ (*cis* slightly more stable with $\Delta E_{cis-trans} = -0.6$) and more pronounced with L^6 ($\Delta E_{cis-trans} = -1.4$ kcal/mol). According to those results, it could be assumed that the *cis* conformation is preferred for $[(MoO_2)_2(L^6)(Im)_2]$ in acetonitrile, unlike for the two other complexes $[(MoO_2)_2(L^{1,5})(Im)_2]$.

28 April 2020. Dovulcaded Dy University of New England 2 9 5 4 0 7 1 0 6 8 2 9 5 4 0 7 In order to unveil the situation in detail, comparisons with other potential intermediates were performed. One part was related to the $\Delta E_{cis-trans}$ for the putative molecules without imidazole molecules, $[(MoO_2)_2(L^i)]$. In the gas phase, the $[(MoO_2)_2(L^i)]$ 38 optimized structures with L^1 and L^5 ligands were very close, 39 $(\Delta E_{cis-trans} = +0.1 \text{ kcal/mol})$, with the *trans* structure being <u>−</u> 240 slightly more stable than the cis one. The situation was reversed <u>4</u>1 with L^6 ($\Delta E_{cis-trans}$ =-1.5 kcal/mol), where the *cis* isomer was 42 more stable. Thus, the gas phase seemed to privilege the cis-43 $[(MoO_2)_2(L^6)]$ structure clearly. With the acetonitrile PCM correction, all $\Delta E_{cis-trans}$ were negative, favouring the cis-44 45 [(MoO₂)₂(Lⁱ)] isomer, with a higher $\Delta E_{cis-trans}$ for L⁶ (-1.3 46 kcal/mol) than for L¹ and L⁵ (-0.8 and -0.2 respectively). Thus, 47 according to the energy difference cis-[(MoO₂)₂(L⁶)] structure 48 seems to be favoured in acetonitrile.

At this point, it is important to comment the relative stability of 49 the intermediate species [(MoO₂)₂(Lⁱ)(Im^{ONO})] (i=1, 5, 6), *i.e.* 50 where one imidazole was added to the starting compounds. In 51 52 all investigated cases, in the gas phase and by using acetonitrile correction, the $\Delta E_{cis-trans}$ were negative with the highest 53 difference established for L⁶. 54

After those simple calculations, it might be concluded that the 55 56 cis/trans conformational preference could be deduced from the 57 energy difference between the different *cis/trans* optimised structures at each step. A minimal energy difference is 58 59 necessary to give a final conclusion. In the case of the non-60

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Scheme 3. Investigated epoxidation reaction.



stabilized species, $\Delta E_{cis-trans}$ <-0.8 (in gas phase) and <+0.1 kcal/mol (in PCM) seems to be enough to predict the cis structure (in both cases, gas phase and PCM correction) while the monosubstituted species need $\Delta E_{cis-trans} < -0.5$ (in gas phase) and <-1.0 (with PCM correction). For the final structures, ΔE_{cis-} $_{trans}$ <+3.0 kcal in the gas phase and < -0.6 kcal with solvent correction. Calculations in the gas phase should not be taken as reference in this case and the addition of the solvent correction is a necessity to have reliable values. It has to be noticed that free energies (Table 1) and enthalpies (ESI, Table S9) give similar trends.

Catalytic studies

Until now, our research has been focused on the catalytic epoxidation of cyclooctene utilising mononuclear molybdenum(VI) complexes derived from hydrazones, under environmentally friendly conditions (emphasis on low catalyst loading, use of aqueous TBHP as oxidant, and no addition of any organic solvent to the reaction mixture).¹⁴ Complexes 1-6 were tested as epoxidation catalysts following the same catalytic protocol (Scheme 3). The polymeric molybdenum(vi) complexes **1–6** afforded cyclooctene conversions in very high yields > 93% (Figure 6).

Selectivity towards the expected product, cyclooctene epoxide, is excellent in all cases, falling in the range of 85–91% (Figure 7). Some subtle effects are observed, especially at the initial phase of the reaction, which can be coupled with structural differences among the ligands. Namely, if 1 (without



Figure 6. Converted cyclooctene vs. time with dioxomolybdenum(vi) (pre)catalysts: 1 – green, 2 – purple, 3 – red, 4 – black, 5 – yellow, 6 - blue. Conditions: Mo/cyclooctene/TBHP(aq) = 1/400/800, T = 80 °C.

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Figure 7. Comparison of selectivity and conversion parameter for cyclooctene epoxidations with Mo catalysts after 5 h of the reaction. Mo/cyclooctene/TBHP(aq) = 1/400/800, T = 80 °C.

substituents on the aromatic rings) is taken as the reference, it seems that incorporation of the hydroxyl group on the aldehyde residue does not influence the catalytic activity, while the inclusion of the methoxy substituents on the same positions slightly decreases it. These effects are different from the ones observed previously for mononuclear Mo(vi) complexes based on ONO ligands,15,16 which can be ascribed partially to the nature of the ligand framework and partially to the presence of two vicinal catalytically active Mo centres (when considering monomeric units). It should be noted that in the organic layer, the one analysed by GC, only the epoxide was detected. However, the water layer of the reaction mixture contained the corresponding diol, which is expected since it has been known that the water can inhibit epoxidation reaction by epoxide ring opening. TOF values after 20 min of the reaction are the highest for the complexes 1-4, reaching values of around 600 for complexes 1, 2, 4, and 823 for complex 3. It should be noted that complex 3, the fastest activated catalyst, is completely dissolved in the reaction media after only 50 min of the reaction, assuming the fastest transformation into the catalytically active pentacoordinated species. In contrast to complexes 1-4, complexes 5 and 6 display the slowest transformation into the active species. However, all the tested catalysts after 5 h provided almost maximal TON values around 390 (Figure 8).





In contrast to the published Mo catalytic systems under the comparable reaction conditions, complexes9/D1146010456 considerably more active and selective towards the epoxide than e.g. dioxomolybdenum polymeric catalysts derived from isonicotinic acid hydrazide.14d) On the other hand, catalytic activity and epoxide selectivity of **1–6** is similar and comparable to the dinuclear dioxomolybdenum systems derived from aminobenzhydrazides and alike aldehydes.^{14b),c)} Although the presence of water can inhibit the reaction and promote epoxide opening to the corresponding diol, avoiding the addition of the organic solvent to the reaction mixture and using oxidant in an aqueous form, offers great benefits in the context of an environmentally acceptable process. By comparison with the classical process using m-CPBA in organic solvent where the treatment after reaction does need tedious post-treatment, producing high quantity of waste,²⁹ the use of aqueous TBHP is appealing since the by-product (t-BuOH) is an important chemical feedstock that can be easily separated by distillation and further used in the industry. After all, green metrics³⁰ support and justify the proposed epoxidation protocol (E-factor close to zero and atom economy of 63% for the presented process vs. 44% for the *m*-CPBA one and a better mass recovery parameter than the *m*-CPBA procedure).

Conclusions

The presented work highlights the proficiency of carbohydrazides, as flexible two-compartment ligands, and reliability of the dioxomolybdenum(VI) core MoO₂²⁺ in the design of the discrete and extended metal-organic architectures. This combination seems to be particularly beneficial for the development of modular structures that are based on oligonuclear building blocks. As our results clearly demonstrate the same [(MoO₂)₂L] tectons can afford either discrete complexes, through the coordination of the capping moieties (methanol or imidazole), or polymeric ensembles by the association of the fragments via Mo=O···Mo interactions. Subsequently, such structural modularity allows the formation and interconversion between them to be controllable under appropriate reaction conditions. Furthermore, structural flexibility as established for the imidazole-based systems, which display cis and trans isomers, as opposed to methanolcontaining monomeric complexes, where solely -cis arrangements are observed, offers a solid platform for shapedirected development of more complex systems, either discrete (molecular cages) or extended ones (coordination polymers). Finally, the catalytic efficiency of here investigated systems provides a good starting point for further development of comparable systems, both homometallic and heterometallic ones. In that respect, our future studies will be focused on indepth analysis and the comparison of synergic and antagonistic effects imposed by the two metal centres.

Experimental data

Synthetic procedures

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Ligands were prepared by the reaction of carbohydrazide with an appropriate aromatic aldehyde in methanol in molar ratio 1:2, as described in the literature.¹⁰ Except for H_4L^6 , the remaining ligands were previously reported. Carbohydrazide, 2-hydroxy-1-naphthaldehyde, salicylaldehyde, 2,3dihydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 2hydroxy-3-methoxybenzaldehyde and 2-hydroxy-4methoxybenzaldehyde were commercially available and were used without further purification. The starting compound [MoO₂(acac)₂] was prepared as described in the literature.³¹

Preparation of H₄L⁶. 2-hydroxy-4-methoxybenzaldehyde (0.17 g, 1.1 mmol) was added to a methanolic solution of carbohydrazide (0.05 g, 0.55 mmol in 20 mL). The mixture was heated under reflux for 2 hours and then cooled to room temperature. The obtained product was filtered and dried. Yield: 0.154 g, 77%. Selected IR data (cm⁻¹): 3360–2800 (O–H), 1706 (C=O), 1634–1604 (C=N), 1290 (C_{ar}–O).

Synthesis of polymeric compounds

 $[MoO_2(acac)_2] (0.11 g, 0.34 mmol) was added to a solution of the appropriate carbohydrazide derivative, H_4L^{1-6}, in dry acetonitrile (0.17 mmol in 100 mL or 250 mL in the case of H_4L^4). The mixture was stirred and heated at 65 °C for 2 h (H_4L^{1-3, 5-6}) or 20 h (H_4L^4). The obtained product was filtered and dried.$

44 $[(MoO_2)_2(L^4)]_n$ (4). Yield: 65.0 mg, 71%. Anal. Calcd. for 45 $C_{15}H_{10}Mo_2N_4O_9$ (582.14): C, 30.95; H, 1.73; N, 9.62%. Found: C, 31.08; 46 H, 1.75; N, 9.75%. TG: calcd. for MoO_3, 49.45%, found: 49.62%. 47 Selected IR data (cm-1): 1590, 1574 (C=N), 1223 (C-O), 926, 898 49 (Mo=O), 796, 781 (Mo=O···Mo).

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Preparation of discrete dinuclear complexes DOI: 10.1039/D0NJ01045F

Complexes with coordinated methanol. [MoO₂(acac)₂] (0.11 g, 0.34 mmol) and 4,4'-bipyridine (5 mg, 0.03 mmol) were added to a solution of the appropriate carbohydrazide derivative, $H_4L^{1,5,6}$, in methanol (0.17 mmol in 20 mL). The mixture was stirred and refluxed for 2 h. The obtained product was filtered and dried.

[(MoO₂)₂(L¹)(CH₃OH)₂] (1a). Yield: 47.8 mg, 46%. TG: calcd. for MoO₃, 46.87%, found: 48.25%; calcd. for CH₃OH, 10.43%, found: 9.81%. Selected IR data (cm⁻¹): 3320 (O_{MeOH}-H), 1594, 1557 (C=N), 1268 (C-O), 1016 (C_{MeOH}-O), 928, 904, 892 (Mo=O).

$$\label{eq:constraint} \begin{split} & \hbox{[(MoO_2)_2(L^6)(CH_3OH)_2](6a). Yield: $51.7 mg, 45\%. TG: calcd. for MoO_3, $42.70\%, found: $43.16\%; calcd. for CH_3OH, 9.50\%, found: $8.88\%. $$ Selected IR data (cm^{-1}): $3210 (O_{MeOH}-H), 1595 (C=N), 1244 (C-O), $1016 (C_{MeOH}-O), 925, 890 (Mo=O). $$ \end{split}$$

Complexes with coordinated imidazole. $[MoO_2(acac)_2]$ (0.11 g, 0.34 mmol) and imidazole (0.045 g, 0.66 mmol) were added to a solution of the appropriate carbohydrazide derivative, $H_4L^{1,5,6}$, in acetonitrile (0.17 mmol in 20 mL). The mixture was stirred and heated at 65 °C for 2 hours. The obtained product was filtered and dried.

 $\label{eq:loss} $ [(MoO_2)_2(L^1)(Im)_2]$ CM_3CN (1b CH_3CN). Yield: 36.8 mg, 32\%. TG: calcd. for MoO_3, 39.58\%, found: 43.42\%; Selected IR data (cm^{-1}): 1593, 1557 (C=N), 1266 (C-O), 932, 915, 906, 885 (Mo=O). $ \end{tabular}$

[(MoO₂)₂(L⁵)(Im)₂]·CH₃CN (5b·CH₃CN). Yield: 36.8 mg, 32%. TG: calcd. for MoO₃, 36.56%, found: 36.92%. Selected IR data (cm⁻¹): 1591, 1558 (C=N), 1254 (C−O), 927, 904, 886, 871 (Mo=O).

 $\label{eq:characteristic} $ [(MoO_2)_2(L^6)(Im)_2]$ - 2CH_3CN (6b+2CH_3CN). Yield: 36.8 mg, 32\%. TG: calcd. for MoO_3, 34.75\%, found: 35.12\%; calcd. for CH_3CN, 9.91\%, found: 8.44\%. Selected IR data (cm^{-1}): 1599, 1560 (C=N), 1263 (C-O), 932, 918, 904, 888 (Mo=O). $ \end{tabular}$

Solid-state transformations (grinding) of dinuclear complexes **1a**, **5a'-0.64CH₃OH** and **6a** were performed with agate mortar and pestle by hand.

Physical methods

TG analysis was carried out with a Mettler-Toledo TGA/SDTA851e thermobalance using aluminium crucibles. All experiments were recorded in a dynamic oxygen atmosphere with a flow rate of 100 cm³ min⁻¹. Heating rates of 10 K min⁻¹ were used for all investigations.

Elemental analyses were provided by the Analytical Services Laboratory of the Ruđer Bošković Institute, Zagreb.

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FT-IR spectra were recorded on a Perkin Elmer Spectrum Two FTIR Spectrometer using Attenuated Total Reflectance technique (ATR).

NMR spectra were recorded on Bruker Avance III HD 400 spectrometer operating at 400 MHz. Compounds were dissolved in DMSO- d_6 and measured in 5 mm NMR tubes at 298 K with TMS as an internal standard. The sample concentration was 10 mg/mL.

The powder X-ray diffraction data for qualitative phase analysis (ESI, Figure S41-S43) were collected by the Phillips X'Change powder diffractometer in the Bragg-Brentano geometry using Cu K_{α} radiation. The sample was contained on a Si sample holder. Patterns were collected in the range of $2\theta = 4-40^{\circ}$ with the step size of 0.03° and at 0.8 s per step. The data were collected and visualized using the X'Pert programs Suite.

Chromatograms were obtained using Agilent 7820A chromatograph with an FID detector and HP5-MS capillary column (30 m × 0.32 mm × 0.25 μ m). The GC parameters were quantified with authentic samples of the reactants and products. Conversion of olefins and formation of corresponding epoxides and diols were calculated from calibration curves ($R^2 = 0.999$) relative to acetophenone as an internal standard (ESI, Figure S44).

General procedure for the epoxidation of cyclooctene by aqueous

TBHP. In a typical reaction, cyclooctene (2.76 mL, 20 mmol), aqueous TBHP (70% w/w, 40 mmol) and acetophenone (0.1 mL) and molybdenum (pre)catalyst, 0.25 mol % [Mo], were used, and the reaction mixture was stirred for 5 h at 80 °C. The reaction was monitored by withdrawing small aliquots at certain time intervals and analysing them by GC.

DFT calculations

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All calculations were carried out with the Gaussian 09 rev. D01 program suite,³² with the DFT approach using the B3LYP threeparameter functional³³ in conjunction with the 6-31G* basis set³⁴ for the light atoms (O, N, C, H) plus the CEP-31G set for the Mo atom.³⁵ The geometry of all complexes was optimized from the geometry determined by X-ray diffraction without any symmetry constraint (ESI, Table S10). Frequency analysis confirmed that the optimized geometries of all the stable compounds were local minima. Thermochemical corrections were obtained at 298.15 K on the basis of frequency calculations, using the standard approximations (ideal gas, rigid rotor and harmonic oscillator). Solvent effects were included by means of PCM single point calculations on the gas-phase optimized geometries.³⁶

X-Ray crystallography. Single crystal diffraction.

High-quality single crystals of the ligand H₄L⁶, methanol basedcomplexes **1a**, **5a**·**CH**₃**OH**, **5a**'**·0.64CH**₃**OH**, **6a** and the imidazolebased ones **1b**·**CH**₃**CN**, **5b**·**CH**₃**CN**, **6b**·**2CH**₃**CN**, were grown from the corresponding reaction mixtures. Diffracted intensities were collected on Oxford Diffraction Xcalibur 3 diffractometer using Mo K_{α} radiation ($\lambda = 0.71073$ Å) using ω -scans. Data were prepared using the *CrysAlis Pro* program package.³⁷ A summary of general and crystal data, intensity data collection and final refinement parameters are presented PPE\$9,19362015121976 structures were solved with dual space methods using SHELXT.³⁸ The refinement procedure by full-matrix leastsquares methods based on F^2 values against all reflections included anisotropic displacement parameters for all non-H atoms. Hydrogen atoms bound to carbon atoms were placed in geometrically idealized positions and refined by the use of the riding model with $U_{iso} = 1.2U_{eq}$ of the connected carbon atom or as ideal CH₃ groups with $U_{iso} = 1.5U_{eq}$. Hydrogen atoms attached to oxygen atoms (O1 in H₄L⁶; O8, O9, O17 and O18 in **1a**; O10, O11 and O12 in 5a·CH₃OH; O10, O11A and O11B in 5a'·0.64CH₃OH; O10 and O11 in 6a) and nitrogen atoms (N2 in H_4L^6 ; N6 and N8 in **1b·CH₃CN**; N8 in **5b·CH₃CN**; N6 and N8 in 6b-2CH₃CN) were located in the difference Fourier maps at the final stages of the refinement procedure. Their coordinates were refined freely but with restrained N–H distances of 0.86(2) (H₄L⁶) or 0.88(2) (1b·CH₃CN, 5b·CH₃CN, 6b·2CH₃CN) and O-H distances of 0.82(2) (H₄L⁶, **5a·CH₃OH**, **6a**), 0.83(1) (**1a**) or 0.84(2) Å (5a·0.64CH₃OH). All refinements were performed using SHELXL-2013.³⁹ The SHELX programs operated within the Olex2 suite.⁴⁰ Geometrical calculations and molecular graphics were done with Mercury.41

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Table of Contents Entry

Discrete and polymeric ensembles based on dimolybdenum(vi) units with adaptive carbohydrazide ligands are described. The polymeric complexes are efficient catalysts for cyclooctene epoxidation under eco-friendly conditions.

