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Solubilizing dimolybdenum paddlewheel complexes for energy storage applications†

Simon G. Gersib, S. M. Supundrika Subasinghe [ID] and Neal P. Mankad [ID] *

Three paddlewheel-type Mo≡Mo complexes incorporating the solubilizing carboxylate ligands 2-(2-methoxyethoxy)acetate, isovalerate, and 5-methylhexanoate were prepared and characterised for potential use in energy storage applications. Along with a previously reported compound, the series demonstrates control over properties including solubility, reduction potential, and Li$^+$ binding in electrolytes relevant to Li batteries.

Molecular coordination compounds are used in energy storage research to design new electrodes, electrolytes, and electrolyte additives.[1,2] These applications rely on the tunability of coordination complexes to optimize parameters such as redox behaviour, catalytic activity, charge and ion transport properties, and solubility. Therefore, further advances may be enabled by exploration of classes of coordination compounds underutilized in energy storage. During our studies of second coordination sphere effects on Mo≡Mo quadruple bonds,[3] we recently discovered[4] that the paddlewheel-type dimolybdenum compound, Mo$_2$(mea)$_4$ [**1**, mea = 2-(2-methoxyethoxy)acetate, Fig. 1a], is effective as an electrolyte additive for Li metal batteries.[5] The poly(ether) substituents of **1** were found to bind Li$^+$ ions from the electrolyte, forming cationic aggregates that self-assemble on the Li metal surface. Upon immobilisation, the additive influenced surface chemistry by passivating the Li metal towards parasitic reactions with the electrolyte while maintaining or enhancing charge transport through the solid-electrolyte interphase,[6] ultimately leading to improved robustness toward calendar aging without notable sacrifice in performance.[4]

During those studies, we found that seemingly obvious control experiments such as replacement of Mo$_2$(mea)$_4$ with the canonical Mo$_2$(OAc)$_4$ that lacks Li$^+$ binding groups were impractical due to inherently low solubility of many paddlewheel structures.[7] Furthermore, for continued examination of electrolyte additive effects, it is necessary to synthesise new derivatives based on **1** that enable tuning of properties such as redox potential and Li$^+$ binding ability, in addition to solubility. Here, we report three new Mo≡Mo compounds that demonstrate control of these properties relevant to energy storage, adding to the already extensive literature of dimolybdenum paddlewheels that have been historically important to fundamental knowledge of structure and bonding.[8,9] Establishing these synthetic protocols meets a requirement for further research in energy storage with this class of compounds, which will be reported in due course.

We began this set of studies by targeting derivatives based on Mo$_2$(OAc)$_4$ that replaced acetate ligands with more solubilizing carboxylates and/or had lower molecular symmetry (and, thus, lower crystallinity). Since poly(ether) substituents are known to solubilize coordination complexes,[10–12] the candidate we identified in our previous study was Mo$_2$(mea)$_4$ (**1**).[4] A second candidate we targeted was Mo$_2$(isoval)$_4$ (**2**, isoval = isovalerate), which is based on commercially available isovaleric acid. Our third target was heteroleptic *cis*-Mo$_2$(mea)$_2$(DAniF)$_2$ (**3**, DAniF = *N*,*N*′-bis(*p*-anisyl)formamidinate). Lastly, we also synthesised Mo$_2$(mha)$_4$ (**4**, mha = 5-methylhexanoate). These four structures are shown in Fig. 1a.

Like previously studied **1**,[4] we were able to synthesise **2** and **4** in single-step procedures from Mo(CO)$_6$ and isovaleric acid or 5-methylhexanoic acid at gram scale in excellent yields based on a published Mo$_2$(OAc)$_4$ preparation.[13] Complex **3** was successfully synthesised by adapting a literature preparation of *cis*-Mo$_2$(OAc)$_2$(DAniF)$_2$.[14] New complexes **2**, **3**, and **4** were characterised by X-ray crystallography (Fig. 1b). The Mo≡Mo distances in these complexes span a small range (Table 1) quite similar to the reported value of 2.093(1) Å for Mo$_2$(OAc)$_4$.[15] Like previously reported structures of **1**,[4] the solid-state structure of **3** was characterised as a LiBF$_4$ adduct. The structure features Li$^+$ ions captured by the mea ligands in an overall 2 : 1 Li : Mo$_2$ stoichiometry. Each Li$^+$ ion is chelated

Department of Chemistry, University of Illinois Chicago, Chicago, IL 60607, USA. E-mail: npm@uic.edu
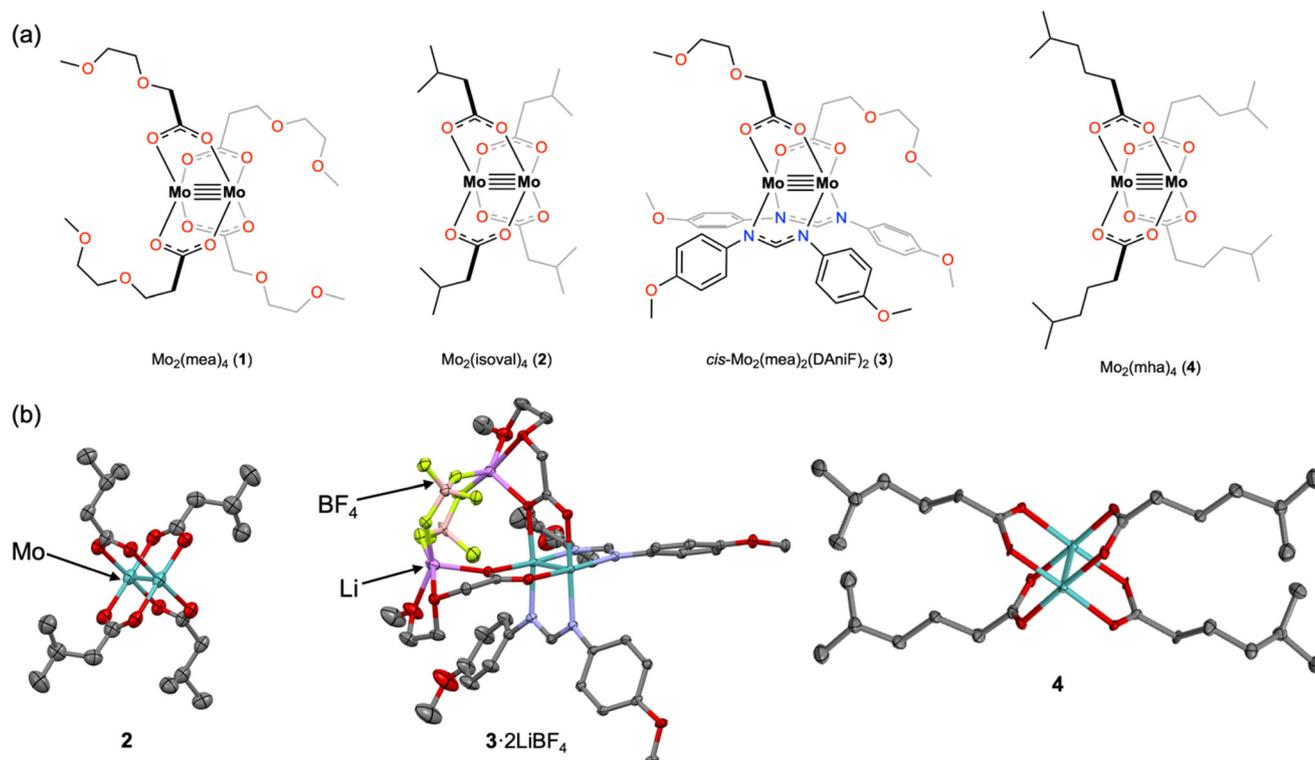
Fig. 1 (a) Dimolybdenum molecules probed in this study. (b) Solid-state structures of $Mo_2(isoval)_4$ (**2**), cis-$Mo_2(mea)_2(DAniF)_2$·$2LiBF_4$ (**3**·$2LiBF_4$), and $Mo_2(mha)_4$ (**4**) determined by X-ray crystallography (50%-probability thermal ellipsoids, H atoms omitted).

Table 1 Selected properties of the compounds in this study

| Complex	$d_{Mo≡Mo}$ (Å)	DME solubility (mM)	$E_{1/2}$ (mV vs. Fc^+/Fc)[a,b]
$Mo_2(mea)_4$ (**1**)	2.09891(16)[c]	302 ± 13	100[c]
$Mo_2(isoval)_4$ (**2**)	2.0926(9)	81.9 ± 6	16
cis-$Mo_2(mea)_2(DAniF)_2$ (**3**)	2.097(1)[d]	436 ± 13	−150
$Mo_2(mha)_4$ (**4**)	2.0897(4)	214 ± 14	−48
$Mo_2(OAc)_4$	2.093(1)[e]	Insoluble	10[f]

[a] Determined using a ferrocene internal standard. [b] Electrolyte: 0.5 M LiTFSI/DME. [c] From Gersib et al.[4] [d] For **3**·$2LiBF_4$. [e] From Robbins et al.[15] [f] Electrolyte: 0.5 M NBu_4PF_6 in CH_2Cl_2.

by two ether oxygens and one carboxylate oxygen from mea. The coordination sphere of each Li^+ ion is completed by BF_4^- anions that each bridge between the two Li^+ ions. Unlike **1**, which forms extended one-dimensional (1D) chains in the solid state,[4] the structure of **3** is a discrete molecular entity.

Solubility data in 1,2-dimethoxyethane (DME, monoglyme), a relevant solvent for metal battery experiments,[4] for all four complexes is shown in Table 1 and range from <0.1 M (**2**) to approaching 0.5 M (**3**). For comparison, $Mo_2(OAc)_4$ was found to be completely insoluble in DME. Qualitatively, all new complexes **1–4** also showed solubility in tetrahydrofuran (THF). Complexes **1**, **3**, and **4** showed significant solubility in acetonitrile, while **2** was only sparingly soluble. Generally, the solubility trend is **3** > **1** > **4** ≫ **2** ≫ $Mo_2(OAc)_4$. From this (albeit

limited) dataset, one can conclude that increased chain length, solubilizing carboxylate ligands, and lowered molecular symmetry all assist with solubilizing δ-bonded paddlewheel complexes based on the $Mo_2(OAc)_4$ motif.

Cyclic voltammetry (CV) data for all four complexes in 0.5 M LiTFSI/DME [TFSI = $N(SO_2CF_3)_2$] are shown in Fig. 2. Each
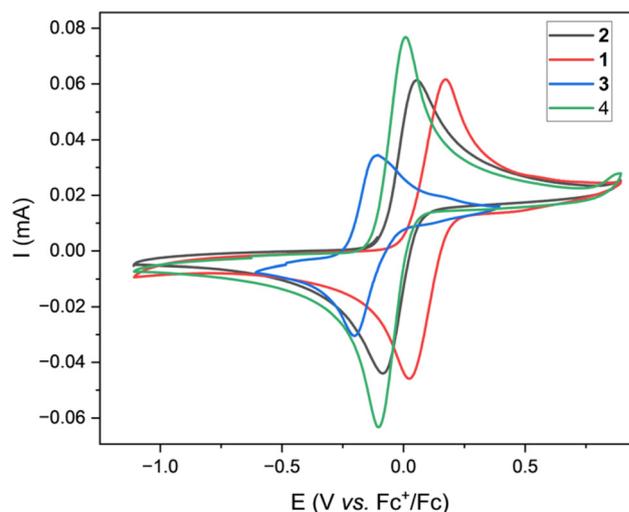
Fig. 2 Cyclic voltammetry of complexes **1–4** (0.5 M LiTFSI/DME, 100 mV s^{-1}).

(quasi-)reversible redox wave is assigned to a Mo_2^{5+}/Mo_2^{4+} couple based on ample literature precedent.[8,9] The $E_{1/2}$ values reported in Table 1 highlight how sensitive the δ-bond's energy level is to the coordination environment. (Although we were unable to measure the CV for $Mo_2(OAc)_4$ in the same electrolyte, its $E_{1/2}$ value in a different electrolyte is quite similar to that of **2** as expected.) As we have shown in a previous study,[4] the shift to positive potentials for **1** relative to $Mo_2(OAc)_4$ likely derives from the presence of Li^+ ions in the second coordination sphere. On the other hand, the shift to negative potentials for **3** relative to $Mo_2(OAc)_4$ is due to a well-known primary coordination sphere effect of substituting acetates for more electron-donating amidinates,[8,9] which is expected to be of a larger magnitude (and of opposing sign) than the second-sphere charge effect of Li^+ binding.[3] Compared to **1** and **3**, the $E_{1/2}$ values for complexes **2** and **4** are similar to $Mo_2(OAc)_4$ and span a range of just 64 mV.

Initially, we assumed that the Mo_2^{5+}/Mo_2^{4+} potential for **3** might shift to more negative potentials in the absence of Li^+ ions in the electrolyte. Therefore, we conducted CV experiments at constant 1 M ion concentration but with varying Li^+ concentration over 0–1000 mM (Fig. S4†). Surprisingly, there was negligible effect of $[Li^+]$ on $E_{1/2}$, with all values spanning a range of only ~15 mV (Fig. S5 and S6†). By comparison to previous data for **1**[4] and for Mo_2 complexes with quaternary ammonium cations in the second coordination sphere,[3] it can be concluded that **3** coordinates Li^+ with a very low binding constant such that there is effectively no population of $3·Li^+$ in the solution-phase CV experiments despite the presence of $LiBF_4$ in the crystal structure. This is a notable difference between complexes **1** and **3** despite their both containing multiple mea ligands.

In conclusion, we have synthesised and characterised three new paddlewheel-type Mo≡Mo complexes for potential use in energy storage applications, motivated by our recent results with $Mo_2(mea)_4$ (**1**). Through variation of the bridging carboxylate structures and implementation of heteroleptic ligation, the series of complexes demonstrates tunability with respect to solubility, reduction potential, and Li^+ binding constant. Application of these complexes as electrolyte additives and for other purposes will be reported in due course.

Author contributions

All authors contributed to conceptualization, data visualization, and writing. S. G. G. and S. M. S. S. conducted all investigations. N. P. M. acquired funds and supervised.

Conflicts of interest

There are no conflicts to declare.

Data availability

Crystallographic data for compound **2–4** have been deposited at the CCDC under deposition numbers 2420431–2420433† and can be obtained from https://www.ccdc.cam.ac.uk. All other data supporting this article have been included as part of the ESI.†

Acknowledgements

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