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Synthesis and Characterization of $[Mo_3S_4(NDABu)(HNDABu)_2]^{3-}$ and $[Mo_3S_4(HNDAPr)_3]^{2-}$ Anions as Building Blocks for Organic–Inorganic Hybrid Solids

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The polymetallic cation $[Mo_3S_4(H_2O)_9]^{4+}$ was used as an inorganic precursor to generate new hybrid organic–inorganic chalcogenide clusters. Three organic compounds with flexible and hanging arms were synthesized and investigated as ligands for coordination complexes with the rigid and electroactive inorganic $\{Mo_3S_4\}$ unit. Interestingly, the $\{Mo_3S_4\}$ core formed hybrid structures with the flexible H_3NDABu [*N*-(3-carboxypropyl)iminodiacetic acid] and H_3NDAPr [*N*-(2-carboxyethyl)iminodiacetic acid] ligands, which were characterized by X-ray crystallography. Surprisingly, no crystals were isolated, when the more rigid H_3NDABn [*N*-(4-methoxycarbonylbenzyl)iminodiacetic acid] ligand was used. The two coordination complexes $[Mo_3S_4(NDABu)(HNDABu)_2]^{3-}$ and $[Mo_3S_4(HNDAPr)_3]^{2-}$ were characterized by X-ray diffraction (XRD), IR spectroscopy, thermal gravimetric analysis (TGA), ^1H NMR spectroscopy, elemental analysis, and electrochemistry. The organic ligands H_3NDABu, H_3NDAPr, and H_3NDABn were characterized by XRD, IR, HR mass, and ^{13}C and ^1H NMR spectroscopy. $[Mo_3S_4(NDABu)(HNDABu)_2]^{3-}$ and $[Mo_3S_4(HNDAPr)_3]^{2-}$ constitute promising preformed building blocks to generate new organic–inorganic hybrid molecular or extended materials.

Introduction

Organic–inorganic hybrid materials represent a wide and versatile class of compounds with potential applications ranging from medicine and biology[1] to catalysis,[2] gas storage or separation,[3,4] electrical conductivity,[5] and magnetism.[6] Investigations concerning the structure, design, and control of the architecture have become major challenges in this field. The main goals are always to obtain compounds with the required structures and properties and to start from well-designed building blocks. During the last decade, much work has been devoted to the synthesis of such materials through the modification of organic ligands and inorganic clusters.[7,8] In this context, polyoxometalate (POM) clusters were revealed as good inorganic building blocks because of the diversity in their composition, shape, size, and charge.[9] Triangular chalcogenide-bridged clusters such as $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo or W) are also good candidates to generate organic–inorganic hybrid materials.[10] We previously described the use of the triangular chalcogenide-bridged cluster $[Mo_3S_4(HNTA)_3]^{2-}$ (NTA^{3-} = nitrilotriacetate) as a preformed building block to generate metal–organic materials.[11] Interestingly, this cluster contains three hanging carboxylates and six carbonyl functions that are available for further coordination to an electrophilic species. The 3D networks, which result from the cluster $[Mo_3S_4(HNTA)_3]^{2-}$ and the La^{3+} cation, $La_2Cl[Mo_3S_4(NTA)_3]\cdot 17H_2O$[12] and $La_{0.75}Cl_{0.25}[Mo_3S_4(HNTA)_3]\cdot 18H_2O$[13] have been described. Under mild synthetic conditions (room temperature and ambient pressure), the hanging carboxylate functions are not coordinated with the La^{3+} cations in $La_{0.75}Cl_{0.25}[Mo_3S_4(HNTA)_3]\cdot 18H_2O$. In contrast, in the 3D network $La_2Cl[Mo_3S_4(NTA)_3]\cdot 17H_2O$, which is obtained under hydrothermal synthesis conditions, the free carboxylate functions are coordinated to the La^{3+} cations. The self-condensation process of the $[Mo_2O_2S_2(OH_2)_6]^{2+}$ cation in the presence of the structuring agent $[Mo_3S_4(HNTA)_3]^{2-}$ allowed us to isolate the largest oxothiomolybdenum ring, which consists of an {Mo18} cyclic arrangement built around.[14] These first results undoubtedly demonstrated the potential of this cluster $[Mo_3S_4(HNTA)_3]^{2-}$ and its derivatized species as valuable

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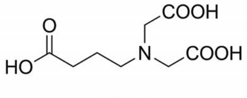
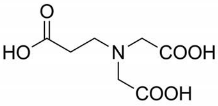
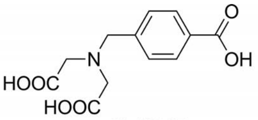


H_3NDABu



H_3NDAPr



H_3NDABn

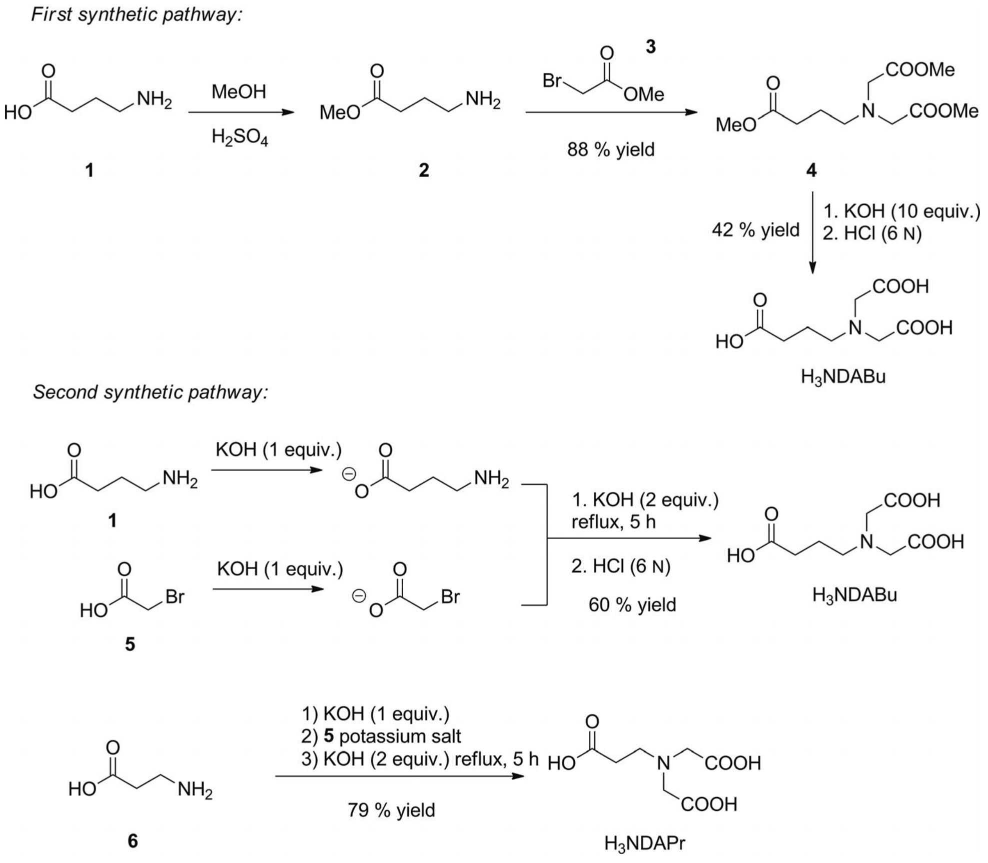
preformed building blocks. In light of these promising results, we aimed to modify the cluster by varying its organic part and to determine how the resulting metal–organic material and its corresponding properties could be affected by this modification. To obtain some further insight about the influence of the spacer in the organic part, we chose to investigate a series of H_3NTA analogues with notably two ligands with flexible alkyl chains, that is, H_3NDABu [*N*-(3-carboxypropyl)iminodiacetic acid], H_3NDAPr [*N*-(2-carboxyethyl)iminodiacetic acid], and the more rigid H_3NDABn [*N*-(4-methoxycarbonylbenzyl)iminodiacetic acid], which incorporates an aromatic ring in its backbone.

The syntheses and structures of the organic precursors to H_3NDABu, H_3NDAPr, and H_3NDABn as well as of the resulting coordination complexes $[Mo_3S_4(NDABu)(HNDABu)_2]^{3-}$ and $[Mo_3S_4(HNDAPr)_3]^{2-}$ are described. The synthesis of $[Mo_3S_4(HNDABn)_3]^{2-}$, which includes a more rigid spacer, is also reported.

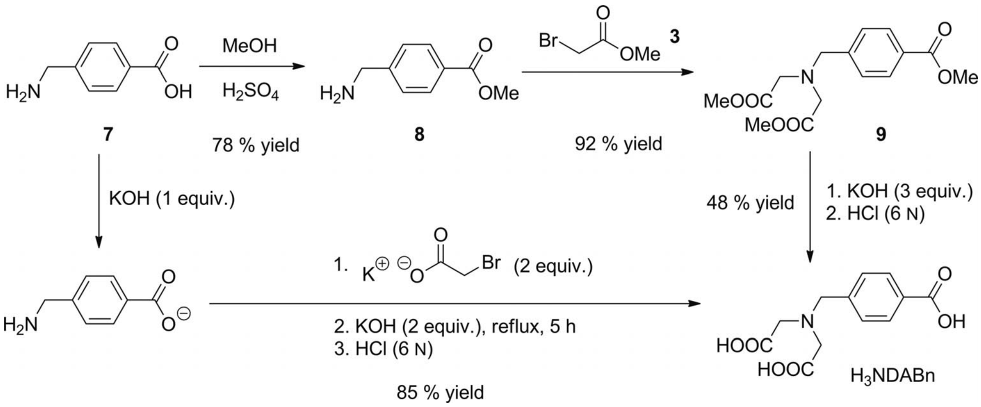
Results and Discussion

Synthesis of the Ligands

The three ligands H_3NDABu, H_3NDAPr, and H_3NDABn were prepared by *N*-alkylation of the corresponding amino acids. Two synthetic pathways were investigated for the synthesis of the ligand H_3NDABu. The first one involved a three-step approach in which 4-aminobutyric acid (**1**) was esterified first under acidic conditions with methanol to give methyl 4-aminobutyrate (**2**), which underwent *N*-alkylation upon treatment with 2 equiv. of methyl bromoacetate (**3**, see Scheme 1). Finally, under basic conditions, the hydrolysis of triester **4** furnished the tripodal ligand H_3NDABu in low yield. Surprisingly, the cleavage of the three ester groups in **4** proved to be more difficult than anticipated, and the synthesis of the ligand could only be accomplished by using a large excess amount of potassium



Scheme 1. Two pathways investigated for the H_3NDABu and H_3NDAPr syntheses.



Scheme 2. Synthesis of H_3NDABn.

hydroxide. Thus, H_3NDABu was recovered contaminated with a non-negligible amount of potassium chloride. This problem was resolved in the second strategy in which the *N*-alkylation of the terminal amine was successfully achieved without the protection of the acid groups.[15] The desired ligand H_3NDABu was isolated in pure form in 60% yield by the direct reaction under basic conditions between bromoacetic acid and 4-aminobutyric acid. By using this second synthetic approach, H_3NDAPr was prepared from 3-aminopropanoic acid (**6**) and obtained with a much higher yield (79%) than previously reported (60%).[16] By using a procedure similar to that of the first synthetic approach for H_3NDABu, the third ligand H_3NDABn was prepared in three steps starting from 4-(aminomethyl)benzoic acid (**7**, see Scheme 2).

To assess the effective structure of the three organic ligands, suitable crystals of H_3NDABr, H_3NDABu, and H_3NDABn were obtained by slow concentration of mixed solutions of methanol and water, and the X-ray solid-state structures were determined (see Figure 1).

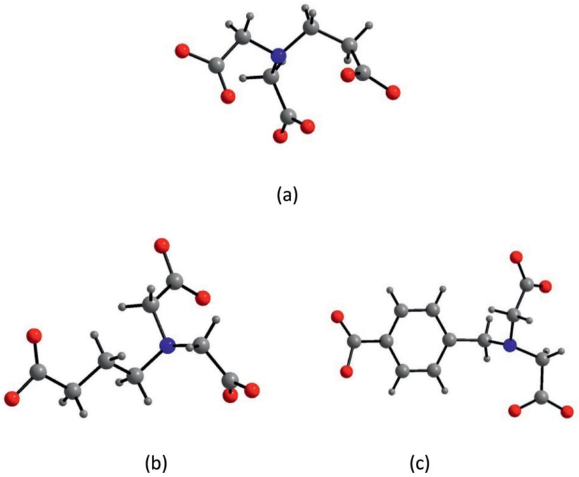


Figure 1. Views of (a) H_3NDAPr, (b) H_3NDABu, and (c) H_3NDABn as ball-and-stick representations (C = grey, N = blue, O = red).

The three ligands were then engaged in a reaction with the inorganic $\{Mo_3S_4\}$ unit. Typically, the addition of a basic solution of the tricarboxylic ligands to an acidic solution of $(NH_4)_2[Mo_3S_4Cl_6(H_2O)_3]$ provided the clusters $[Mo_3S_4(NDABu)(HNDABu)_2]^{3-}$ (**C1**) and $[Mo_3S_4(HNDAPr)_3]^{2-}$ (**C2**) in approximately 40% yield from H_3NDABu and H_3NDAPr, respectively; the cluster $[Mo_3S_4(HNDABn)_3]^{2-}$ (**C3**) was provided in 60% from the more rigid H_3NDABn ligand. Crystals suitable for X-ray crystal structure analyses were obtained for the two clusters **C1** and **C2**; **C3** was not soluble enough to isolate crystals and record NMR spectra. It was characterized by IR spectroscopy, thermal gravimetric analysis (TGA), elemental analysis, and ESI-MS.

Structures of the Coordination Complexes

The X-ray crystallographic study of **C1** revealed that the structure consists as a discrete trianionic cluster with two sodium cations and one cesium cation. The unit cell also contains nine water molecules. For **C2**, the X-ray diffraction (XRD) study revealed that the structure consists of a discrete dianionic cluster with one sodium cation and one potassium cation. This unit cell also contains water molecules.

The structures of the anions are shown in Figure 2, and the selected interatomic distances and angles for the two anions are collected in Table 1. The triangular core $\{Mo_3S_4\}$ of the anions in which each molybdenum atom is octahedrally coordinated by three sulfur atoms along with one nitrogen and two oxygen atoms from the ligand presents classical bond lengths and angles (see Table 1).[10] For **C1**, two of the free hanging carboxylate ligands are protonated, as shown by lengths of carbon–oxygen distances that are different in ligands **A** and **B** [C–O range: 1.209(8)–1.326(7) Å] and nearly equal in ligand **C** [C–O 1.260(7) and 1.265(7) Å]. Bond valence sum calculations on the three molybdenum atoms belonging to the central cluster show evidence of a +IV oxidation state for each atom (for $Mo_{\mathbf{A}}$ ca. 4.03, $Mo_{\mathbf{B}}$ ca. 3.99, and $Mo_{\mathbf{C}}$ ca. 3.99). Thus, the central cluster charge is $\{Mo_3S_4\}^{4+}$. If we take account of the three countercations in the global charge, one hanging carboxylate group of the complex has to be deprotonated to assure the neutrality of the species, as shown by the average distances of both of the C–O bonds in the functional group (1.260 Å and 1.265 Å).[16] For **C2**, one of the free carboxylate groups is found disordered, and the two others are protonated [C–O range: 1.252(1)–1.221(1) Å]. This was confirmed by XRD analysis, which revealed two cations for **C2**. We obtained only a few crystals of **C2**; however, NMR and IR spectroscopy as well as TGA and elemental analyses were performed on the most abundant powder of $Na_2[Mo_3S_4(HNDAPr)_3]·8H_2O$.

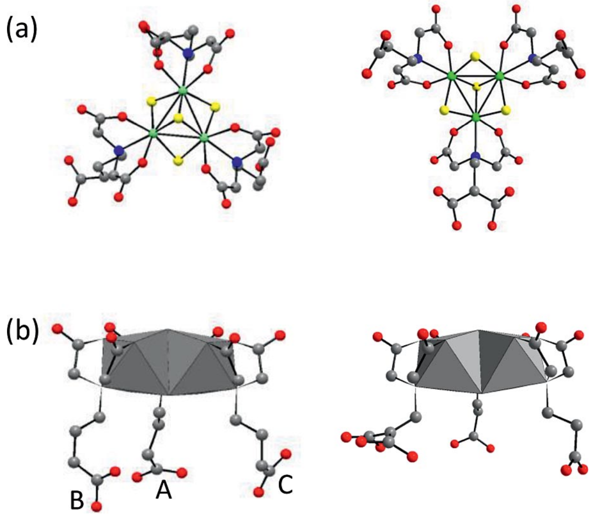


Figure 2. Views of the $[Mo_3S_4(NDABu)(HNDABu)_2]^{3-}$ (**C1**) and $[Mo_3S_4(HNDAPr)_3]^{2-}$ (**C2**) anions: (a) ball-and-stick representation showing the octahedral coordination of the molybdenum atoms (C = grey, N = blue, O = red, S = yellow, Mo = green); (b) mixed polyhedral ball-and-stick representation of the free hanging carboxylate groups.

Table 1. Selected interatomic distances [Å] and angles [°] for $Na_2Cs[Mo_3S_4(NDABu)(HNDABu)_2]·9H_2O$ (**C1**) and for $NaK[Mo_3S_4(HNDAPr)_3]·3.5\ H_2O$ (**C2**).

Distances [Å] and angles [°]	C1	C2
Mo–Mo	2.7421(7)–2.7521(7)	2.7533(6)–2.7641(8)
Mo–(μ_3S)	2.335(1)–2.345(1)	2.325(1)–2.334(2)
Mo–(μS)	2.284(1)–2.299(1)	2.291(1)–2.306(1)
Mo–N	2.290(5)–2.298(4)	2.305(5)–2.317(7)
Mo–O	2.119(4)–2.147(4)	2.112(4)–2.140(4)
Mo–(μ_3-S)–Mo	71.75(4)–72.02(4)	72.46(1)–72.94(1)
Mo–(μ-S)–Mo	73.48(4)–73.87(5)	73.64(1)–73.79(4)

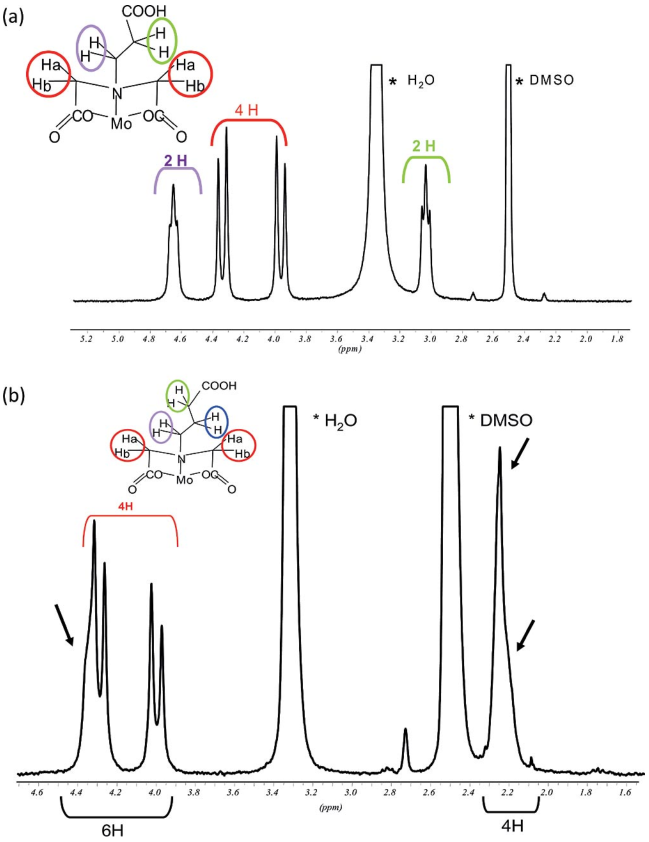


Figure 3. ^1H NMR spectra in $[D_6]DMSO$ of (a) $[Mo_3S_4(HNDAPr)_3]^{2-}$ (**C2**) and (b) $[Mo_3S_4(NDABu)(HNDABu)_2]^{3-}$ (**C1**).

The ^1H NMR spectrum in $[D_6]DMSO$ of **C1** contains the signals of the coordinated H_3NDABu ligand (see Figure 3b). The two doublets centered at δ = 4.35 and 4.00 ppm are attributed to the coupled diastereotopic protons (J = 16.0 Hz) of the two methylene groups belonging to the acetate fragments coordinated to the $\{Mo_3S_4\}$ moiety.

The singlet at δ = 2.15 ppm (12 H) is due to two of the methylene groups of the free hanging carboxylate, and the remaining signal for the third methylene group is overlapped with the doublet at δ = 4.35 ppm. The ^1H NMR spectrum in DMSO of **C2** (see Figure 3a) shows two triplets at δ = 4.65 and 3.03 ppm (J = 6.4 and 7.4 Hz) corresponding to the two methylene groups of the free hanging carboxylate. The two doublets centered at δ = 4.32 and 3.96 ppm (J = 15.7 Hz) are attributed to the coupled diastereotopic protons of the methylene groups belonging to the acetate fragments coordinated to the $\{Mo_3S_4\}$ moiety.

The IR spectra of **C1** and **C2** show two types of carboxylate groups, that is, those attached to the $\{Mo_3S_4\}$ core and the free hanging carboxylates, which are revealed at 1631 cm^{-1} by a strong absorption with a shoulder at 1529 cm^{-1}, respectively, for **C1** and at 1716 (shoulder) and 1625 cm^{-1} (strong absorption), respectively, for **C2**. Other absorptions can be assigned as the ν_{as}(OCO) of the nitriloacetic ligands. The ν_s(OCO) are observed at 1465 and 1390 cm^{-1} and 1462 and 1389 cm^{-1}, respectively, for **C1** and **C2**. For **C3**, only one type of carboxylate group is observed with absorptions at 1614 and 1385 cm^{-1}. Several absorptions between 600 and 400 cm^{-1} could be attributed to ν(Mo–S).

The electrochemical properties of compounds **C1** and **C2** were studied by cyclic voltammetry in a pH = 7 buffer and, under the same conditions, were compared with those of $[Mo_3S_4(NTA)_3]^{5-}$. As previously reported in the literature, all of the compounds exhibited one reversible redox couple assigned to the first reduction state of the $\{Mo_3S_4\}$ cluster.[11,14] The redox potentials $E°$ (mean values between the cathodic and anodic peak potentials) are very similar for the three compounds {–0.55 V for $[Mo_3S_4(NTA)_3]^{5-}$,

–0.57 V for $[Mo_3S_4(NDAPr)_3]^{5-}$, and –0.61 V for $[Mo_3S_4(NDABu)_3]^{5-}$}, which is evidence of the weak influence of the ligands on the reduction of Mo^{IV} and of a purely metal-centered reduction process (see Figure 4).

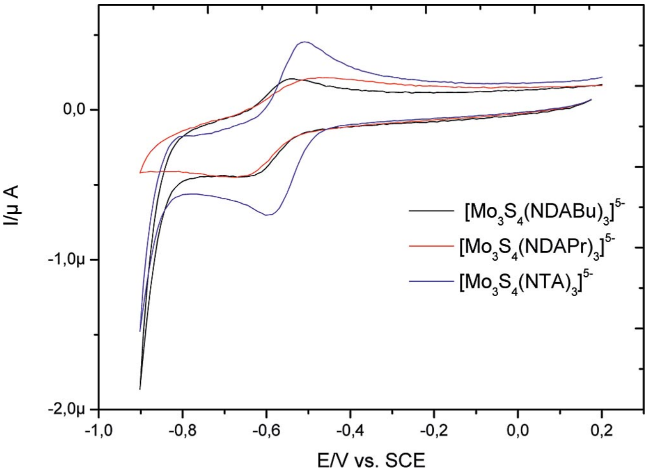


Figure 4. Cyclic voltammograms of 0.2 mM solutions of deprotonated clusters $[Mo_3S_4(NDABu)_3]^{5-}$, $[Mo_3S_4(NTA)_3]^{5-}$, and $[Mo_3S_4(NDAPr)_3]^{5-}$ obtained at pH = 7 [0.5 M Li_2SO_4 + 0.2 M tris(hydroxymethyl)aminomethane + H_2SO_4] with a potential range from +0.2 V to –0.9 V. The scan rate was 10 mV s^{-1}. The working electrode was glassy carbon, and the reference electrode was SCE (saturated calomel electrode).

Conclusions

A series of iminodiacetic acid derivatives have been prepared and investigated as new hanging arms for hybrid organic–inorganic clusters. The two new clusters $Na_2Cs[Mo_3S_4(NDABu)(HNDABu)_2]\cdot 9H_2O$ and $NaK[Mo_3S_4(HNDAPr)_3]\cdot 3.5H_2O$ were synthesized and characterized. In future work, attempts to coordinate the remaining free carboxylates to various transition metals will be carried out for the construction of 3D networks. Coordination of these clusters to other metals could generate heterometallic hybrid clusters with new capabilities.

Experimental Section

Characterization Techniques: Elemental analyses were performed by the Service Central d'Analyse du CNRS. Mass spectrometry was performed by the Spectropole of Aix-Marseille University (Marseille). ESI mass spectral analyses were performed with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HR mass spectral analyses were performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. The water content corresponding to the weight loss up to about 250 °C was determined by TGA using a TGA-7 Perkin–Elmer apparatus. The ^1H and ^{13}C NMR spectroscopic data were recorded at room temperature in 5 mm o.d. tubes with either a Bruker Avance 300 spectrometer equipped with a QNP probe head or a Bruker Avance 400 spectrometer (Spectropole, Aix-Marseille University; ^1H NMR at 400 MHz, ^{13}C NMR at 100 MHz). The ^1H and ^{13}C NMR chemical shifts were referenced to the $CDCl_3$ solvent peak at $\delta = 7.26$ and $\delta = 77.0$ ppm, respectively. Infrared spectra were recorded with an FTIR Magna 550 Nicolet spectrophotometer by using the technique of pressed KBr pellets.

X-ray Crystal Structure Determination: Intensity measurements for **C1** were carried out with a Bruker X8 diffractometer equipped with a CCD bidimensional detector using monochromatized Mo-K_α radiation (λ = 0.71073 Å). Selected crystal data and details of the data collection for the cluster are given in Table 2. An absorption correction was applied by using the SADABS program[17] based on the Blessing method.[18] The structures were solved by direct methods followed by Fourier difference syntheses using the SHELXTL package. All atoms, with the exception of the hydrogen atoms, were anisotropically refined. The final reliability factors converged to R_1 = 0.0356 and wR_2 = 0.0903. Selected interatomic distances [Å] are given in Table 1. Intensity measurements for H_3NDABu, H_3NDAPr, H_3NDABn, and $NaK[Mo_3S_4(HNDAPr)_3]\cdot 3.5H_2O$ were carried out with an Agilent Supernova diffractometer equipped with a CCD bidimensional detector by using monochromatized Cu-K_α radiation (λ = 1.54184 Å). Selected crystal data and structure refinement details are given in Table 2. Analytical numeric absorption corrections by using a multifaceted crystal model were made on the basis of expressions derived by Clark and Reid.[19] The structures were solved by direct methods (SHELXS[20] or SIR97[21] programs) followed by Fourier difference syntheses using the SHELX package.[19] CCDC-866115 (for **C1**), -886520 (for H_3NDABu), -886521 (for H_3NDAPr), -886522 (for H_3NDABn), and -886523 (for **C2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Data: These were obtained with an EG & G 273 A driven by a PC with the M270 software. A one-compartment cell with a standard three-electrode configuration was used for the cyclic voltammetry experiments. The composition of the supporting electrolyte was 0.5 M Li_2SO_4 + 0.2 M tris(hydroxymethyl)aminomethane + H_2SO_4 at pH = 7. The concentration of the clusters was 0.2 mM. Prior to each experiment, the solutions were deaerated thoroughly for at least 30 min with pure argon, and a positive pressure of this gas was maintained during subsequent work. All cyclic voltammograms were recorded at a scan rate of 10 mV s^{-1}, unless otherwise stated. All of the experiments were performed at room temperature, which was controlled and set for the laboratory at 20 °C. The reference electrode was a saturated calomel electrode (SCE), and platinum gauze with a large surface area was used as a counter electrode. Both electrodes were separated from the bulk electrolyte solution by fritted compartments filled with the same electrolyte. The working electrode was a 3 mm o.d. glassy carbon disc (GC, Le Carbone de Lorraine, France).

Synthesis Procedures: The precursors $(NH_4)_2[Mo_3S_4Cl_6(H_2O)_3]$ and $Na_2[Mo_3S_4(HNTA)_3]\cdot 7H_2O$ were synthesized according to previously reported procedures without any modifications and with similar yields.[11] All of the reagents were purchased from Aldrich and Alfa Aesar with the best purity available and used as received. Methyl 4-aminobutanoate (**2**) was prepared according to a literature procedure.[22]

Methyl 4-[Bis(2-methoxy-2-oxoethyl)amino]butanoate (4): To a solution of methyl 4-aminobutanoate (**2**, 0.70 g, 6 mmol) in absolute ethanol were successively added methyl bromoacetate (**3**, 1.13 mL, 12 mmol) and potassium carbonate (1.24 g, 9 mmol), and the reaction mixture was heated at reflux for 24 h. The solution was filtered to remove the excess amount of K_2CO_3, and the solid was washed with diethyl ether. The solution was transferred back to a round-

Table 2. Crystal and structure refinement data for H_3NDABu, H_3NDAPr, H_3NDABn, $Na_2Cs[Mo_3S_4(NDABu)(HNDABu)_2]·9H_2O$ (**C1**), and $NaK[Mo_3S_4(HNDAPr)_3]·3.5H_2O$ (**C2**).

	H_3NDABu	H_3NDAPr	H_3NDABn	**C2**	**C1**
Empirical formula	$C_8H_{13}NO_6$	$C_7H_{11}NO_6$	$C_{12}H_{13}NO_6$	$C_{21}H_{30}KMo_3N_3NaO_{23.50}S_4$	$C_{24}H_{50}CsMo_3N_3Na_2O_{27}S_4$
Temperature [K]	180	180	180	298	100
Wavelength [Å]	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
Crystal size	0.41 × 0.19 × 0.10	0.32 × 0.15 × 0.12	0.25 × 0.09 × 0.05	0.21 × 0.15 × 0.09	0.16 × 0.08 × 0.02
Space group	$P2_1/c$	$P2_1/c$	$Pbca$	$Cmca$	$P2_1/c$
a [Å]	14.1353(2)	5.43300(10)	26.1283(3)	15.0340(4)	17.6609(7)
b [Å]	12.2120(2)	13.7838(3)	6.67291(9)	26.9497(5)	12.5186(5)
c [Å]	6.51379(9)	12.0704(3)	27.6461(4)	22.6446(5)	21.7666(9)
α [°]	90	90	90	90	90
β [°]	92.1575(14)	107.261(2)	90	90	110.631(2)
γ [°]	90	90	90	90	90
V [Å^3]	1123.62(3)	863.21(3)	4820.13(11)	9174.7(4)	4503.7(3)
Z	4	4	16	8	4
$D_{cald.c}$ [g cm^{-3}]	1.627	1.579	1.473	1.707	2.001
μ [mm^{-1}]	4.425	1.220	1.024	9.922	1.916
θ limits [°]	3.13/73.37	5.00/73.37	3.20/73.45	3.28/73.30	1.23/25.00
Reflections collected	6336	3114	10821	11100	57585
Independent reflections	2205	1691	4727	4687	7824
R(int)	0.0209	0.0107	0.0214	0.0330	0.0704
Final R indices	R_1 = 0.0279	R_1 = 0.0327	R_1 = 0.0369	R_1 = 0.0683	R_1 = 0.0356
[$I > 2\sigma(I)$]	wR_2 = 0.0733	wR_2 = 0.0832	wR_2 = 0.0954	wR_2 = 0.2146	wR_2 = 0.0903
R indices	R_1 = 0.0285	R_1 = 0.0339	R_1 = 0.0459	R_1 = 0.0732	R_1 = 0.0603
(all data)	wR_2 = 0.0737	wR_2 = 0.0840	wR_2 = 0.1019	wR_2 = 0.2265	wR_2 = 0.1055
Data/restraints/parameters	2205/0/167	1691/0/139	4727/0/388	4687/1/277	7824/0/579
Residual electron density [e Å^{-3}]	0.273/–0.364	0.260/–0.200	0.242/–0.266	2.904/–1.412	0.998/–0.677
Goodness-of-fit	1.106	1.111	1.027	1.371	1.087

bottomed flask, and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (SiO_2, CH_2Cl_2/acetone) to give the triester (1.38 g, 88 %) as a light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 6 H), 3.68 (s, 3 H), 3.56 (s, 4 H), 2.76 (t, 2 H, J = 6.1 Hz), 2.40 (t, 2 H, J = 7.3 Hz), 1.80 (q, 2 H, J = 7.1 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9, 171.6, 54.7, 53.4, 51.5, 31.3, 23.1 ppm. HRMS (ESI): calcd. for $[M + H]^+$ 262.1285; found 262.1287.

4-[Bis(carboxymethyl)amino]butanoic Acid (H_3NDABu)

(a) Hydrolysis of 4: To a solution of KOH (9 g, 225 mmol) in H_2O (25 mL) and ethanol (25 mL) was added **4** (8.36 g, 32 mmol), and the solution was heated at reflux for 48 h. After removal of the volatiles, the remaining aqueous layer was acidified to pH = 5 with a diluted aqueous HCl solution. The aqueous phase was extracted with diethyl ether (3 × 100 mL) to remove all of the organic impurities. The aqueous phase was concentrated to dryness in a rotary evaporator. To remove the potassium chloride, the white solid was recrystallized several times from methanol. The title compound (2.95 g, 42 %) was obtained as a white solid.

(b) Direct Synthesis from 4-Aminobutanoic Acid (1): Bromoacetic acid (**5**, 7.24 g, 53 mmol) in H_2O (50 mL) was neutralized by adding KOH (3.24 g, 55 mmol) under nitrogen at room temperature over a period of 20 min. To this solution was added **1** (2.68 g, 26 mmol), which was neutralized with KOH (1.53 g, 26 mmol). The mixture was heated at reflux under nitrogen for 5 h, and KOH (3.14 g, 53 mmol) was added over the first 30 min of heating. The solution was cooled to room temperature, and the pH was adjusted to 6 by the addition of HCl (6 M solution). The solution was concentrated under vacuum, until a white precipitate of potassium salts appeared. The solid was removed by filtration, and the pH of the resulting solution was adjusted to 2.5 by the addition of HCl (6 M solution). After several days, the product precipitated from the solution. The precipitate was removed by filtration and recrystallized from water to give H_3NDABu (6.97 g, 60 %). ^1H NMR (400 MHz, D_2O): δ = 3.74 (s, 4 H), 3.19 (t, J = 7.8 Hz, 2 H), 2.28 (t, J = 7.0 Hz, 2 H), 1.98–1.75 (m, 2 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 180.1, 170.6, 57.0, 55.9, 33.3, 20.4 ppm. IR: $\tilde{\nu}$ = 324 (w), 352 (w), 556 (m), 702 (m), 914 (m), 959 (w), 988 (w), 1103 (w), 1208 (m), 1711 (C=O, sh), 1628 (br. s) 1581 (sh), 1473 (sh), 1400 (s), 1362 (sh), 1332 (m) cm^{-1}. HRMS (ESI): calcd. for $[M - H]^-$ 218.0670; found 218.0669.

3-[Bis(carboxymethyl)amino]propanoic Acid (H_3NDAPr): Compound **5** (7.36 g, 53 mmol) in H_2O (50 mL) was neutralized by adding KOH (3.24 g, 58 mmol) under nitrogen at room temperature over a period of 20 min. To this solution was added 3-aminopropanoic acid (**6**, β-alanine, 2.32 g, 26 mmol), which was neutralized with KOH (1.53 g, 26 mmol). The mixture was heated at reflux under nitrogen for 5 h, and KOH (3.14 g, 56 mmol) was added over the first 30 min of heating. The solution was cooled to room temperature, and the pH was adjusted to 6.5 by the addition of HCl (6 M solution). The solution was concentrated under vacuum, until a white precipitate of potassium salts appeared. The solid was removed by filtration, and the pH of the resulting solution was adjusted to 2.5 by the addition of HCl (6 M solution). After several days, the product precipitated from the solution, and the precipitate was removed by filtration and then dried under vacuum to give H_3NDAPr (4.2 g, 79 %). ^1H NMR (400 MHz, D_2O): δ = 3.84 (s, 4 H), 3.49 (t, J = 8.1 Hz, 2 H), 2.79 (t, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 174.1, 169.7, 56.9, 51.8, 29.0 ppm. IR: $\tilde{\nu}$ = 1720 (s), 1624 (s), 1462 (m), 1442 (m), 1401 (s), 1377 (s), 1322 (s), 1257 (s), 1181 (m), 979 (m), 955 (m), 853 (m), 809 (m), 697 (m), 598 (w), 543 (w), 476 (w), 427 (w) cm^{-1}. HRMS (ESI): calcd. for $[M + H]^+$ 206.0659; found 206.0654.

Methyl 4-(Aminomethyl)benzoate (8):[23] To a solution of 4-(aminomethyl)benzoic acid (**7**, 10 g, 66 mmol) in methanol (250 mL) was slowly added concentrated H_2SO_4 (2 mL), and the reaction mixture was heated at reflux overnight. After cooling, the solvent was removed under reduced pressure, which yielded a yellowish residue. The residue was neutralized by the addition of a diluted aqueous NaOH solution, and the ester was extracted with ethyl acetate (3× 100 mL). The combined organic phases were dried with magnesium sulfate, and the solvent was removed under reduced pressure. The resulting residue was purified by filtration through a plug of silica gel (ethyl acetate) to give **8** (8.52 g, 78%), which was used in the next step without any further purification. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 7.90 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.1 Hz, 2 H), 3.84 (s, 3 H, OCH_3), 3.80 (s, 2 H, CH_2), 2.50 (br. s, 2 H, NH_2) ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.2 Hz, 2 H), 7.26 (d, J = 8.2 Hz, 2 H), 3.80 (s, 2 H, CH_2), 3.78 (s, 3 H, OMe) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 166.2, 149.8, 129.1, 127.6, 127.2, 51.9, 45.2 ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 148.2, 129.5, 128.3, 126.6, 51.6, 45.8 ppm. HRMS (ESI): calcd. for $[M + H]^+$ 166.0862; found 166.0862.

Methyl 4-{[Bis(2-methoxy-2-oxoethyl)amino]methyl}benzoate (9): To a solution of **8** (1 g, 6 mmol) in absolute ethanol were successively added **3** (1.13 mL, 12 mmol) and potassium carbonate (1.24 g, 9 mmol), and the reaction mixture was heated at reflux for 24 h. The solution was filtered to remove the excess amount of K_2CO_3, and the solid was washed with diethyl ether. The solution was transferred back to a round-bottomed flask, and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (SiO_2, CH_2Cl_2/acetone) to give the triester (1.71 g, 92%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 4 H, NCH_2CO_2Me), 3.62 (s, 6 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.90 (s, 2 H, $PhCH_2N$), 7.39 (d, J = 8.1 Hz, 2 H), 7.91 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.3, 51.8, 53.9, 57.4, 128.6, 129.1, 129.5, 143.5, 166.7, 171.2 ppm. HRMS (ESI): calcd. for $[M + H]^+$ 310.1285; found 310.1285.

4-{[Bis(carboxymethyl)amino]methyl}benzoic Acid (H_3NDABn)

(a) Hydrolysis of 9: To a solution of KOH (9 g, 225 mmol) in H_2O (25 mL) and ethanol (25 mL) was added **9** (10 g, 32 mmol), and the solution was heated at reflux for 48 h. After removal of the volatiles, the remaining aqueous layer was acidified to pH = 5 by the addition of a diluted aqueous HCl solution. The aqueous phase was extracted with diethyl ether (3× 100 mL) to remove all of the organic impurities. The aqueous phase was concentrated to dryness in a rotary evaporator. To remove the potassium chloride, the white solid was recrystallized several times from methanol. The title compound (4.10 g, 48%) was obtained as a white solid.

(b) Direct Synthesis from 7: Compound **5** (7.36 g, 53 mmol) in H_2O (50 mL) was neutralized by adding KOH (3.24 g, 58 mmol) under nitrogen at room temperature over a period of 20 min. To this solution was added **7** (3.93 g, 26 mmol), which was neutralized in H_2O (50 mL) with KOH (1.53 g, 26 mmol). The mixture was heated at reflux under nitrogen for 5 h, and a solution of KOH (3.14 g, 56 mmol) in water (10 mL) was added over the first 30 min of heating. The solution was cooled to room temperature, and the pH was adjusted to 6.5 by the addition of HCl (6 M solution). The solution was concentrated under vacuum, until a white precipitate of potassium salts appeared. The solid was removed by filtration, and the pH of the resulting solution was adjusted to 2.5 by the addition of HCl (6 M solution). The solution was cooled in an ice bath, and the product precipitated after 30 min. The precipitate was removed by filtration and dried under vacuum to give H_3NDABn (5.91 g, 85%). ^{1}H NMR (400 MHz, D_2O): δ = 3.86 (s, 4 H), 4.54 (s, 2 H), 7.63 (d, J = 8.1 Hz, 2 H), 8.04 (d, J = 8.1 Hz, 2 H) ppm. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.38 (s, 4 H), 3.89 (s, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 7.89 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 56.2, 58.3, 130.2, 131.2, 132.7, 133.7, 170.1, 170.8 ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 55.7, 56.8, 128.5, 129.3, 129.7, 144.3, 167.3, 173.2 ppm. IR: $\tilde{\nu}$ = 536 (w), 561 (w), 643 (w), 668 (w), 698 (m), 774 (m), 812 (m), 907 (m), 1014 (w), 1265 (w), 1322 (w), 1386 (s), 1558 (s), 1623 (br. s), 1709 (m) cm^{-1}. HRMS (ESI): calcd. for $[M + H]^+$ 268.0816; found 268.0821.

Synthesis of $Na_2Cs[Mo_3S_4(NDABu)(HNDABu)_2]\cdot 9H_2O$ (C1): To a solution of $(NH_4)_2[Mo_3S_4Cl_6(H_2O)_3]$ (0.25 g, 0.32 mmol) in HCl (2 M solution, 5 mL) was added H_3NDABu (0.3 g, 1.4 mmol) dissolved in a minimal amount of NaOH (4 M solution). The pH was adjusted to 1.5 by the addition of NaOH (4 M solution). The solution was heated at 90 °C for 30 min. Then, the remaining green precipitate was removed by filtration. CsCl (0.3 g, 1.78 mmol) was added to the solution. After a few days at 4 °C, green crystals of $Na_2Cs[Mo_3S_4(NDABu)(HNDABu)_2]\cdot 9H_2O$ (0.2 g, 40%) were isolated. On the TG curve in the temperature range 30–200 °C, the first weight loss of 12.3% corresponds to the nine lattice water molecules in **C1** (calcd. 11.3%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.40–4.25 (m, 12 H), 4.03 (d, J = 15.9 Hz, 6 H), 2.32–2.15 (br. s, 12 H) ppm. ^{1}H NMR (400 MHz, D_2O): δ = 4.74 (s, 6 H), 4.50–4.60 (br. s, 6 H), 4.25 (d, J = 16.5 Hz, 6 H), 2.35 (s, 12 H) ppm. IR: $\tilde{\nu}$ = 457 (w), 493 (w), 531 (w), 626 (w), 766 (w), 788 (w), 916 (m), 981 (w), 1058 (w), 1086 (w), 1231 (w), 1293 (w), 1631 (C=O, br. s), 1529 (sh), 1465 (sh), 1390 (br. s) cm^{-1}. $C_{24}H_{50}CsMo_3N_3Na_2O_{27}S_4$ (1407.61): calcd. C 20.47, H 3.58, Cs 9.45, Mo 20.48, N 2.98, Na 3.27, S 9.11; found C 21.31, H 3.74, Cs 8.91, Mo 20.39, N 3.15, Na 3.01, S 10.01.

Synthesis of $NaK[Mo_3S_4(HNDAPr)_3]\cdot 3.5H_2O$ (C2): To a solution of $(NH_4)_2[Mo_3S_4Cl_6(H_2O)_3]$ (0.5 g, 0.64 mmol) in HCl (2 M solution, 20 mL) was added H_3NDAPr (0.39 g, 1.9 mmol) dissolved in a minimal amount of NaOH (4 M solution). The pH was adjusted to 1.5 by the addition of NaOH (4 M solution). The solution was heated at 90 °C for 30 min. Then, the remaining green precipitate was removed by filtration. After a few days at room temperature, $Na_2[Mo_3S_4(HNDAPr)_3]\cdot 8H_2O$ (0.32 g, 41%) was isolated as a green powder. On the TG curve in the temperature range 30–190 °C, the first weight loss of 11.9% corresponds to the eight lattice water molecules in $Na_2[Mo_3S_4(HNDAPr)_3]\cdot 8H_2O$ (calcd. 11.05%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.65 (t, J = 6.8 Hz, 6 H), 4.33 (d, J = 15.2 Hz, 6 H), 3.95 (d, J = 15.7 Hz, 6 H), 3.03 (t, J = 7.1 Hz, 6 H) ppm. IR: $\tilde{\nu}$ = 459 (w), 483 (w), 555 (w), 756 (w), 901 (w), 913 (w), 934 (w), 955 (w), 978 (w), 1033 (w), 1091 (w), 1210 (w), 1240 (w), 1249 (w), 1297 (w), 1462 (w), 1716 (C=O, sh), 1625 (br. s), 1462 (m), 1389 (br. m), 1362 (sh) cm^{-1}. $C_{21}H_{43}Mo_3N_3Na_2O_{26}S_4$ (1215.61): calcd. C 20.74, H 3.54, Mo 23.68, N 3.46, Na 3.79, S 9.78; found C 20.52, H 3.28, Mo 23.63, N 3.5, Na 3.14, S 10.06. This powder was recrystallized from a solution of KCl (0.1 M), and a few crystals of $NaK[Mo_3S_4(HNDAPr)_3]\cdot 3.5H_2O$ (**C2**) were isolated for X-ray crystal structure analysis.

Synthesis of $Li_2[Mo_3S_4(HNDABn)_3]\cdot 6H_2O$ (C3): To a solution of $(NH_4)_2[Mo_3S_4Cl_6(H_2O)_3]$ (0.2 g, 0.26 mmol) in HCl (2 M solution, 10 mL) was added H_3NDABn (0.22 g, 0.82 mmol) dissolved in a minimal amount of LiOH (1 M solution). The pH was adjusted to 1.2 by the addition of LiOH (1 M solution). The solution was heated at 90 °C for 30 min. The abundant green precipitate was removed by filtration and then was washed with EtOH (2× 20 mL) and dried with Et_2O (2× 20 mL) to give **C3** (0.19 g, 61%). On the

TG curve in the temperature range 30–190 °C, the first weight loss of 8.5% corresponds to the six lattice water molecules (calcd. 8.57%). IR: $\tilde{\nu}$ = 514 (w), 568 (w), 702 (w), 754 (w), 869 (w), 922 (w), 994 (w), 1019 (w), 1115 (w), 1183 (w), 1271 (sh), 1324 (m), 1614 (C=O, br. s), 1385 (br. s) cm^{-1}. $C_{36}H_{45}Li_2Mo_3N_3O_{24}S_4$ (1333.70): calcd. C 32.42, H 3.40, Li 1.04, Mo 21.58, N 3.15, S 9.62; found C 30.52, H 3.28, Li 0.9, Mo 22.63, N 3.5, S 10.06. HRMS (ESI): calcd. for $[M]^{2-}$ 606.3915; found 606.3914.

Supporting Information (see footnote on the first page of this article): FTIR (Figure S1) and TGA curves (Figure S2).

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