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Mono-oxo-bis-dithioveratrol-molybdate – in Solution a Model for Arsenite Oxidase and in the Solid State a Coordination Polymer with Unprecedented Binding Motifs

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Abstract. Mono-oxo-bis-dithioveratrol-molybdate was synthesized, structurally characterized, and investigated with respect to its oxo-transfer activity. The latter was compared with the activity of the analogous tungsten complex. The title complex is a structural model for molybdopterin bearing arsenite oxidase and both complexes catalyze oxo-transfer reactions successfully to 100 % conversion. With the dithioveratrol ligand the oxidation of triphenylphosphine proved to be faster for the tungsten complex, which is untypical. The solid-state structure of the molybdenum complex exhibits an unexpected and very unusual polymeric structural motif consisting of the complex anion mono-oxo-bis-dithioveratrol-molybdate, sodium cations, and methanol. Infinite double-decker strands are formed with sodium bridges between the ether functions of two ligands in one strand and the Mo=O moiety of the second strand.

Introduction

Apart from the typical 3d transition metals with a role in biology as for instance iron, copper, and zinc, there are also examples, where nature resorts to the use of 4d and 5d transition metals. Though molybdenum and tungsten have far less universal roles than the metals listed above, they still perform essential tasks and are found in almost any organism on earth being it bacteria, plants, or human beings.[1] As an exception to the majority of molybdenum enzymes, molybdenum is found in the most atom economic form of the nitrogenases.[2] It is, however, far more prevalent in the active sites of oxidoreductases as so-called molybdenum cofactor (Moco) and catalyzes basically the same reactions as its higher congener tungsten, which is part of almost identical cofactors (WCo) in closely related enzymes. Both, molybdenum and tungsten are responsible for two-electron oxidation or reduction reactions, which are typically accompanied by the transfer of formally one oxygen atom (O^0). In all molybdenum and tungsten dependent oxidoreductases a specific ligand is present: molybdopterin (MPT, see Figure 1). Molybdopterin consists of the pterin part (the outermost two N-heterocycles), the pyrane ring, a phosphate group, which may be even a triphosphate and bind to a second nucleotide as found in some bacteria, and finally the dithiolene moiety, which binds the active site metal.[3] The molybdopterin ligand has proven to be extremely difficult to synthesize with the closest model having been published just recently, though the enzymes have been known for more than forty years.[4] This very advanced model is still not perfectly mimicking every aspect of MPT but it is strikingly similar. This is, however, the result of many years of synthetic research and a huge input of work. In order to synthesize model ligands for MPT reliably, with good yield and with an acceptable amount of work, typically compounds bearing the coordinating dithiolene function and various different substituents on the double bond are considered to model MPT sufficiently enough.

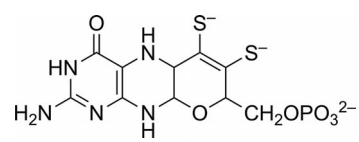

Figure 1. The chemical structure of molybdopterin.

Based on structure homologies and reactivities, the molybdenum and tungsten dependent oxidoreductases have been categorized by *Hille* into different enzyme families in order to facilitate the scientific discussion in this field.[5] For molybdenum, three families were used with the xanthine oxidoreductase and the sulfite oxidase families comprising enzymes, in which the cofactor bears only one MPT. These are typically found in higher organisms. In the DMSO reductase family the cofactor is present with two MPT ligands bound and a coordinating amino acid residue from the surrounding peptide, which constitutes the only covalent interaction between cofactor and peptide. In the oxidized form one oxo ligand is additionally attached to molybdenum. Arsenite oxidase is generally thought to fall into the DMSO reductase family. It is, however, excep-

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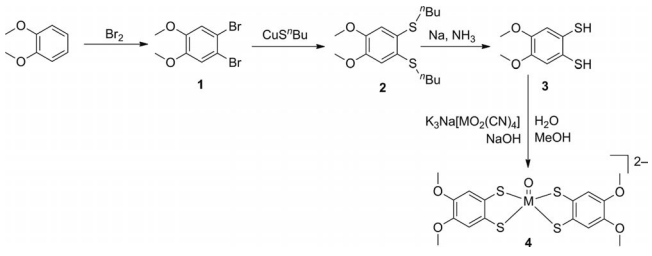
tional as it does not bind directly to the peptide and in place of the amino acid residue an oxo ligand is bound, or two in the oxidized form, respectively.[6] Such composition, i.e. *M*O(dithiolene)$_2$ (*M* = Mo, W) structural motives, are frequently observed in synthetic inorganic chemistry and have been used previously as models for enzymes of the DMSO reductase family.[7]

Our efforts to understand the use of molybdenum and tungsten for the same tasks in very similar and clearly evolutionarily related proteins lead us to synthesize a number of complexes of this composition with both, molybdenum and tungsten, as coordination centers.[8] In a previous study they have been investigated predominantly by electrochemical methods. One such complex-couple was now studied further with respect to its oxo-transfer activity. Furthermore, the synthetic protocol for ligand and complex synthesis was refined and optimized and, most strikingly, the X-ray structure of the molybdenum complex is reported, which crystallizes as an unexpected coordination polymer exhibiting unprecedented binding motifs.

Results and Discussion

Synthesis

The synthesis of both, ligand and complexes, has already been reported[8] but it was refined in the meantime and due to potential pitfalls it is worth to go into more detail than what is currently available. The ligand's synthesis is based on published procedures from the 1970s (Scheme 1).[9] Starting with *o*-dimethoxybenzene a dibromination in 4,5-position is carried out with elemental bromine in dichloromethane. The two bromine substituents are replaced by thioethers via reaction with Cu^{I}-*n*-butylmercaptane. This is used instead of the free *n*-butylthiol since the formation of HBr as side product is not sufficient enough to obtain the desired product in good yield compared to CuBr. CuBr is completely removed from the reaction mixture by thorough extraction with acid, water, and finally ammonia. The free ligand dithioveratrol (vdtH$_2$) (**3**) is obtained by a Birch reduction of the thioether.



Scheme 1. Synthesis of ligand precursor and dithiolene complexes [*M* = Mo (**4**), *M* = W (**5**)].

Free (meaning protonated) dithiolenes are usually rather unstable. If the ene-function is part of a benzene ring, however, they may be reasonably stable as is the case here. In fact the ligand was obtained as crystalline material, of which a structural elucidation was possible, although previous attempts for the same compound have been described as unsuccessful[10].

For the complex synthesis $K_3Na[MO_2(CN)_4]\cdot 6H_2O$ (*M* = Mo, W) is used as precursor, which is dissolved in aqueous NaOH solution. The ligand dissolved in methanol is added and the mixture is heated to 45 °C. It is important to elevate the temperature above room temperature for the reaction to take place but at the same time even higher temperatures tend to destroy the desired products. Careful monitoring of the temperature is therefore required. An immediate color change from blue to brown and eventually to red can be observed. During this reaction the cyanide ligands are replaced by the dithiolenes. In course of this, one of the two oxo ligands, which are in *trans* arrangement in the precursor, is lost. The *trans* arrangement for oxo ligands is decidedly unfavorable and only possible in the precursor due to the significant π-character of the *M*–CN bonds. After the reaction mixture has cooled to room temperature a large-cation source (here benzyl-triethylammonium chloride) is added to precipitate the anionic complexes $[MO(vdt)_2]^{2-}$. Recrystallization from acetonitrile/ethyl ether yields analytically pure complexes. Slow precipitation from the mother liquor, to which only one instead of two equivalents cation were added yields crystalline material, which surprisingly does not contain the bulky ammonium cation but sodium ions instead plus co-crystallized methanol. Recrystallization of the crude product from methanol gives the same product with small instead of large cations present. A bulky ammonium halide is, however, needed to receive a precipitate in the first place. The observation of distinct compositions of the product depending on the solvent used, as indicated by elemental analysis, was unexpected and could only be understood, when the crystal structure of the molybdenum complex crystallized from methanol was solved (see below). The solvent, used to recrystallize, apparently has a significant influence on the composition of the product, which needs to be taken into account for further investigations and reactions of the product from this specific reaction. In order to reproduce the synthesis of the sodium molybdenum complex species the synthetic procedure was modified to abstain from the bulky cation addition. In order to obtain sufficiently pure crystalline material, the reaction product had to be first crystallized from DMF (giving complex **4b** as described in the Experimental Section). From this compound a small amount of the sodium methanol complex **4′** could be obtained again *via* recrystallization from methanol. An analogous coordination polymer with tungsten could not be characterized so far.

The resulting complexes are structural models, for arsenite oxidase in particular, among the molybdenum dependent enzymes and for the tungsten dependent oxidoreductases in general, which mostly bear two molybdopterins in the active sites. In case of the arsenite oxidase the immediate, meaning first and second, coordination sphere is exactly modeled. In case of the tungsten compound the peptide coordination to the active site was neglected. The similarity is however close enough to expect catalytic oxo-transfer activity here as well as for the molybdenum complex. This was investigated by the typical model reaction for oxo transfer.[11]

Oxo-Transfer Catalysis

Complexes **4** and **5** were tested whether they were able to reduce DMSO to DMS and to transfer the respective oxygen atom to the model substrate triphenylphosphine (PPh_3). The reaction typically proceeds via oxygen atom transfer from DMSO to the complex giving a *cis*-dioxo metal complex, which consequently transfers the oxygen to PPh_3. In some previously reported cases the dioxo species (obtained via oxidation by DMSO, Me_3NO, or other oxidizing agents) of similar bis-dithiolene complexes have been isolated and even structurally characterized.[7e,12] PPh_3 as a tertiary phosphine is the substrate of choice due to its good solubility in organic solvents as well as its affinity to oxygen as has been established previously.[11] The reaction progress can be nicely monitored by ^{31}P NMR spectroscopy due to the separate signals of PPh_3 (s, –6 ppm; in [D_6]DMSO) and PPh_3O (s, –26 ppm; in [D_6]DMSO). In course of the reaction the phosphorus atom is performing a nucleophilic attack on the empty Mo=O π^* orbital, while a free electron pair of the oxygen atom is simultaneously attacking the P–C σ^* orbital so that the two-electron reduction of the metal proceeds smoothly.[13] DMSO is commonly used as oxygen source and may be simultaneously employed as solvent and substrate with consequentially very high excess to the catalyst.[14]

Quantification of the formation of PPH_3O out of a tenfold excess of PPh_3 using ^{31}P NMR spectroscopy results in a typical Michaelis-Menten saturation kinetic for the tungsten containing complex (Figure 2, left). A plot of observed concentrations vs. time for the molybdenum complex is shown in Figure 2 right. For both catalysts a 100 % conversion of substrate could be observed.

However, both reactions proceed very slowly, with the tungsten catalyzed reaction needing 102 h to full conversion, whereas the molybdenum mediated reaction requires 107 h. Although for the specific oxo transfer reaction from DMSO to PPh_3 it is more common, that molybdenum complexes are faster catalysts than their tungsten analogues, such behavior is not unprecedented.[15] In this specific case it may come down to a comparably long induction period (up to the first 30 h of reaction) for the molybdenum catalyst. This induction period is possibly caused by the overall slow formation of the oxidized catalyst species $[MoO_2(vdt)_2]^{2-}$ by reaction with DMSO. More measurements with different catalyst-substrate ratios will have to be carried out to reliably determine Michaelis constants, system describing equilibrium constants as well as reaction rate constants for this molybdenum catalyst. Research in this respect is still going on and will be communicated in a follow-up paper.

In contrast to the molybdenum catalyzed reaction, the tungsten mediated reaction shows no induction period and proceeds with zero order kinetics with respect to the substrate PPh_3 until just roughly 31 % of the substrate is left. This corresponds to one of the limiting cases in Michaelis-Menten kinetics, see Equation (1).

$$\frac{d[P]}{dt} = \frac{k_2 \cdot [E]_0 \cdot [S]}{K_M + [S]}$$

$$S >> K_M$$

$$\frac{d[P]}{dt} = k_2\,[E]_0 = V_{sat} \quad (1)$$

The observed rate (V_{sat}) obtained from the slope of the first 70 % of reaction progress equals 2.82×10^{-5} mol·L^{-1} h^{-1}. With a catalyst concentration of 3.38×10^{-4} mol·L^{-1} a first-order rate constant $k_2 = 0.0834$ h^{-1} can be identified. As discussed by *Drexler* et al., the analysis of Michaelis-Menten type kinetics is, in principal, not limited to the initial rate range.[16] The fact that the reaction is running in zero order with respect to the substrate PPh_3 at these little excess amounts of substrate, implies that the Michaelis constant (K_M) has to be very small and the equilibrium between the free catalyst and the substrate lies on the side of the catalyst-substrate complex. The complex pattern of molybdenum catalyzed substrate concentration changes prevents at this point the calculation of kinetic parameters, which could be compared to the tungsten catalyst. What is evident, however, is that the tungsten compound is more efficient, i.e. faster at the investigated conditions. This is most likely caused by molybdenum's reluctance to be oxidized to the Mo^{VI} species as evident from its higher redox potential in analogous compounds, which in turn is based on the stronger relativistic effect in tungsten atoms.[15b,17]

Crystal Structures

As mentioned above, the molybdenum complex could be isolated in two forms depending on the solvent used for recrys-

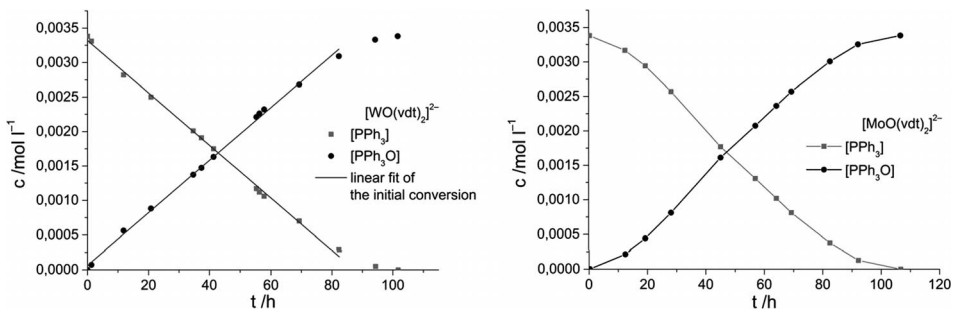


Figure 2. Concentration vs. time diagram of the reaction of 3.38×10^{-4} mol·L^{-1} of **5** (left) and **4** (right) with a tenfold excess of PPh_3 in DMSO at 25.0 °C.

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tallizing the material. The exact composition of the unexpected form of the complex was determined by solving its X-ray structure. Unusual in this case is firstly, that instead of bulky ammonium derived cations the far smaller sodium cations are part of the crystallized material. Secondly, the complex together with its counterion does not form a discrete molecule-ion structure but a coordination polymer consisting of infinite double-decker strands. Figure 3 shows the building blocks of these infinite strands. They consist of two complex molecules, which are arranged in opposite directions but with their apical oxo ligands facing each other. The phenyl rings are arranged in a perfectly parallel orientation (the angle between C1–C6 and C1A–C6A planes equals 0.00°). The oxo ligands are actively involved in holding the two molecules together. Normally, doubly bonded oxo ligands are rather strongly attached to the central metal and are rarely observed to participate in bridging interactions, other than the formation of dimers, by which the double bonds become single bonds. In this case the oxygen atom is directly bound to molybdenum (1.713 Å) and to two sodium ions (2.344 and 2.359 Å). Crystal structures exhibiting such arrangement have so far only been reported for polyoxomolybdates but not for coordination compounds and are generally extremely rare with only two examples among the CCDC entries.[18] Based on the interaction with the two sodium ions the bond length between molybdenum and oxygen is at the longer end of the range typically observed for mononuclear square pyramidal molybdenum complexes with apical oxo ligands but the bond is not exceedingly long.[7i,12g,19]

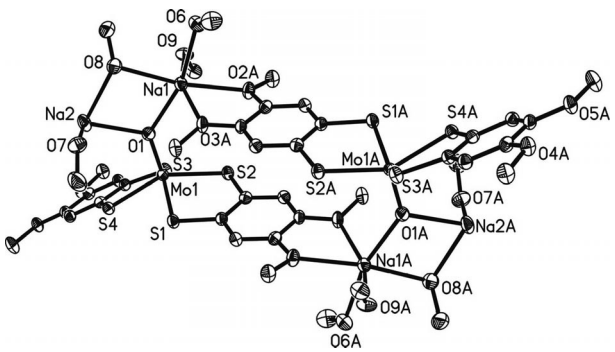

Figure 3. The molecular structure of the smallest unit of the coordination polymer $(Na_2[MoO(vdt)_2]\cdot 4MeOH)_\infty$ (**4′**) consisting of two complex molecules, four sodium ions and eight methanol molecules. Ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity reasons. Selected bond lengths /Å and angles /°: Mo1–O1: 1.713; Mo1–S(1–4): 2.367–2.383; Mo1–Na2: 3.547; Mo1–O1–Na1: 132.88; Mo1–O1–Na2: 120.36; Na1–O1–Na2: 105.53.

In the crystal lattice the double-decker zigzagging strands are arranged parallel to each other forming, from a side view, wavy layers (Figure 4). This is sterically by far the most favorable arrangement for infinite strands and this arrangement is further stabilized by O–H→S hydrogen bonds between one double-decker strand and another as indicated in the Figure for the O8–H to S2 hydrogen bond with 2.522 Å between H and S. Except for one hydrogen bond between a methoxy methyl group (C8) and the lone pair of a methanol oxygen atom (O7) all hydrogen bonds found with the Hbond routine of the platon

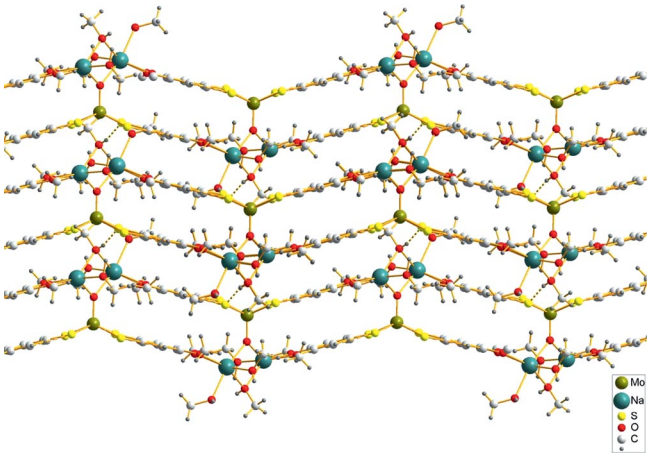

Figure 4. The crystal lattice of $(Na_2[MoO(vdt)_2]\cdot 4MeOH)_\infty$ (**4′**) from a side view. Hydrogen bonds between methanol OH groups and dithiolene sulfurs are indicated as dashed lines for the O8–H to S2 hydrogen bond.

software[20] are those between OH functions and sulfur in a range of 2.28 to 2.53 Å. To the best of our knowledge such hydrogen bonding involvement of dithiolene sulfur atoms has not been observed before and constitutes an unprecedented binding motif for dithiolene complexes of molybdenum and tungsten. A participation of MPT's dithiolene sulfur atoms in hydrogen bonding in the active sites of the enzymes has not been explored so far but, since these hydrogen bonds in the vicinity of molybdenum can exist, it may be worth looking into this from a protein crystallographers point, too.

Turning the crystal lattice around by 90° it becomes clear that the distinct double decker strands are not arranged directly on top of each other but rather in a staggered fashion (Figure 5). If they were arranged directly on top of each other the methanol ligands and the sodium ions of different strands

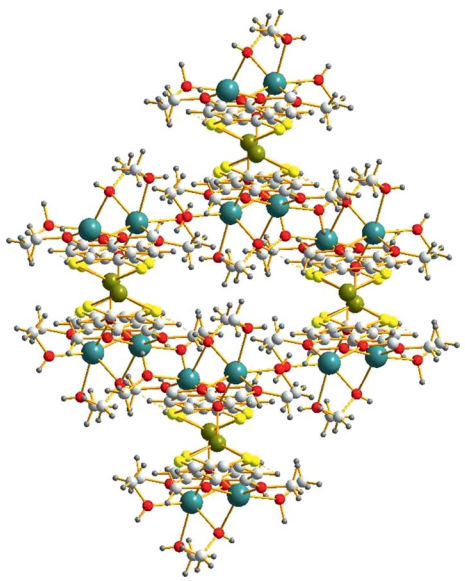

Figure 5. View along four of the double-decker strands in the crystal lattice of $(Na_2[MoO(vdt)_2]\cdot 4MeOH)_\infty$ (**4′**) (one double decker strand left, one right, one on top, one at the bottom).

would collide. It is also evident that the molybdenum atoms of top and bottom single strand are slightly staggered too, presumably to allow a closer contact between the two parts of the double strands.

It was possible to obtain a crystal structure of the free (protonated) ligand too (Figure S1 in the Supporting Information). The ligand crystallizes in the monoclinic space group *C*2/*c* as a merohedral twin and its structure could only be refined to a sufficient *R* value by applying the respective twin law. In comparison with the complex the metric parameters involving sulfur and oxygen atoms, which are interacting with sodium and/or molybdenum ions, are clearly influenced by coordinating the metals.

In the ligand's crystal structure two independent molecules are present in the asymmetric unit. The present four sulfur carbon distances show a significantly larger spread (1.756 to 1.777 Å) than the four sulfur carbon distances in the complex molecule (1.772 to 1.776 Å). The average distance is slightly shorter for the ligand than for the complex, as would be expected (1.768 versus 1.774 Å). This is an indication that by complex formation the metal loosens the sulfur carbon bonds, because electron density is needed for the complex bonds, but also, that overall the electron density around the complex center including the first and second coordination sphere is more evenly distributed via the metal. Regarding the ether oxygen atoms, their oxygen carbon bond lengths are influenced only on the aromatic side by coordinating the sodium cations (which leads to the polymeric structure in the complex's solid state). The aliphatic side of the ether moiety is unperturbed by the coordination with nearly identical average bond lengths and distance spreads for both the complex and the free ligand. This observation is to some extent counterintuitive as the aliphatic side is expected to move with far fewer restrictions than the aromatic phenyl ring. On the aromatic side, the spread in bond lengths is nearly identical for free ligand and complex but the bond lengths have increased in course of the coordination event by about 0.02 Å (averages: ligand = 1.357 versus complex = 1.376 Å). It is possible that not only the coordination of the sodium ions by the ether oxygen atoms contributes to this elongation but also the coordination of molybdenum on the other side of the phenyl ring. Since dithiolenes are non-innocent ligands, this coordination of molybdenum certainly has an influence on the delocalized π electrons throughout the molecule, which in turn may loosen the O–C_{arom} bonds opposite to the sulfur donors even further than only the sodium coordination would do.

Conclusions

Two complexes (molybdenum and tungsten) with the veratroldithiolene ligand were synthesized based on published procedures. Since they can be considered structural models for the immediate coordination sphere of molybdenum and tungsten cofactors with two molybdopterin ligands, they were also tested with respect to functional catalytic oxo transfer ability. Both complexes catalyze the oxygen atom transfer from DMSO to PPh_3 up to a 100% conversion with the tungsten complex being more efficient. The molybdenum complex when recrystallized from methanol forms a coordination polymer, in which two unusual binding motifs were observed: firstly the bridging interaction of the oxo ligand on molybdenum with two sodium ions and secondly the participation of dithiolene sulfur atoms in hydrogen bonding with methanol hydroxy groups.

Experimental Section

General: The Birch reduction and all manipulations dealing with molybdenum containing species were carried out in a nitrogen atmosphere using standard Schlenk techniques. Starting materials were purchased and used as received.

Ethyl ether was distilled from sodium benzophenone ketyl immediately prior to use. Methanol and ethanol were distilled from magnesium turnings prior to use, $CDCl_3$ and acetonitrile from CaH_2.

$K_3Na[MoO_2(CN)_4]\cdot 6H_2O$ and complexes **4** and **5** were prepared according to published procedures.[8,21] The ligand and ligand precursors were prepared based on published procedures.[9]

Synthesis of 1,2-Dimethoxy-4,5-dibrombenzene (1): Bromine (29,7 mL) was added to a solution of 1,2-dimethoxybenzene (40.0 g, 0.29 mol) in dichloromethane (10 mL) at 5.0 °C during 6 h. After leaving the mixture warming up to room temperature overnight in an open flask, the dichloromethane had evaporated and the red-brown precipitate was dissolved in ethyl ether and washed afterwards twice with 2 M NaOH (150 mL) and twice with distilled water (150 mL). The product was sucked dry and recrystallized from methanol yielding 34.66 g (40.38%) of off white needles. **^{1}H NMR** (200 MHz, $CDCl_3$-[d_1], 25 °C, TMS): δ = 3.83 (s, 6 H, OCH_3), 7.03 (s, 2 H, H_{arom}) ppm.

Synthesis of 4,5-Dimethoxy-1,2-bis(*n*-butylthio)benzene (2): This procedure follows mainly the procedure given by *Adams* et al. in 1973: 1,2-dimethoxy-4,5-dibrombenzene (0.025 mol, 7.4 g) and freshly prepared cuprous *n*-butylmercaptide (0.055 mol, 8.4 g) were dissolved in pyridine (8 mL) and) quinoline (8 mL) and heated to 170 °C under reflux for 3.5 h. The reaction mixture was poured into a mixture of ice (150 g) with concentrated HCl (40 mL). After extraction with ethyl ether and washing twice with 10% HCl, once with water and twice with concentrated NH_3, and drying over potassium carbonate eventually a dark orange oil was received (4.87 g, 79.10% yield). An additional recrystallization with ethanol was working well yielding large colorless crystals. **^{1}H NMR** (200 MHz, $CDCl_3$-[d_1], 25 °C, TMS): δ = 0.98 (t, 6 H, CH_3-butyl), 1.51 (sextet, 4 H, CH_2–CH_3), 1.66 (quin, 4 H, CH_2–CH_2–CH_3), 3.06 (t, 4 H, S–CH_2), 3.92 (s, 6 H, OCH_3), 7.32 (s, 2 H, H_{arom}) ppm.

Synthesis of 4,5-Dimethoxybenzene-1,2-dithiol (3): As a typical Birch reduction this reaction is carried out in liquid ammonia in a nitrogen atmosphere. A solution of 4,5-dimethoxy-1,2-bis(*n*-butylthio)benzene (4.87 g, 0.0154 mol) in ethyl ether was added to liquid ammonia in a 500 mL Flask. Portionwise addition of sodium (2.26 g, 0.0985 mol) resulted in the typical color change to dark blue and stirring was continued for 45 min. The reaction was quenched by cautious addition of NH_4Cl (0.77 g, 0.00504 mol) and the ammonia evaporated in a stream of nitrogen. The dark residue was dissolved in MeOH (5 mL) and water (10 mL). After filtration and acidification with concentrated HCl solution a dark green residue was obtained and (re-) crystallized from ethyl ether to give yellow crystals (1.27 g, 25.32% yield). The observed chemical shifts in the NMR spectra are very sim-

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ilar to those published by *Garner* et al. for the corresponding lithium salt, in particular the ^{13}C-NMR values.[10] **^{1}H NMR** (200 MHz, $CDCl_3$-[d_1], 25 °C, TMS): δ = 2.41 (s, 2 H, SH), 4.08 (s, 6 H, OCH_3), 5.62 (s, 2 H, H_{arom}). **^{13}C NMR** (75 MHz, $CDCl_3$-[d_4], 25 °C, solvent): δ = 56.1 (s, *C*H_3), 114.4 (s, *C*H), 122.2 (s, *C*SH), 148.2 (s, *C*O) ppm.

Synthesis of Na_2[MoO(vdt)$_2$] (4b): A solution of 4,5-dimethoxybenzene-1,2-dithol (0.3 g, 1.5 mmol) in methanol (10 mL) was added to a blue solution of $K_3Na[MoO_2(CN)_4]\cdot 6H_2O$ (0.34 g, 0.7 mmol) and NaOH (0.65 g, 16.25 mmol) in degassed water (20 mL). An immediate color change to brown and an increase in temperature was observed. Warming up to 45.0 °C and stirring for 15 min resulted in a further color change to red, while the solution became inhomogeneous. After cooling to room temperature the light blue solution was taken off with a syringe and the remaining red precipitate was washed once with methanol. Dissolving in DMF (4 mL) gave a red solution, which was layered with diethyl ether to form a red microcrystalline material, which was used for the NMR-measurements (see below). Yield: 0.39 g, 23.6 %.

Recrystallization of **4** or **4b** from methanol results in the coordination polymer $(Na_2[MoO(vdt)_2]\cdot 4MeOH)_\infty$ (**4′**), the structure of which could be determined crystallographically. **^{1}H NMR** (300 MHz, MeOD-[d_4], 25 °C, referenced versus solvent): δ = 3.82 (s, 6 H, CH_3), 7.29 (s, 2 H, CH). **^{13}C NMR** (75 MHz, MeOD-[d_4], 25 °C, referenced versus solvent): δ = 56.9 (O*C*H_3), 85.26 (*C*H), 113.73 (*C*–S), 117.61 (C–O) ppm.

Other Physical Measurements: NMR spectra were recorded with either a Bruker Avance 500 spectrometer (500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C) or a Bruker Avance 200 (200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C). ^{1}H-NMR spectroscopic shifts are reported in parts per million (ppm) and referenced to the residual proton resonance of the deuterated solvent ($CDCl_3$ ^{1}H: δ = 7.24 ppm, ^{13}C: 77.0 ppm) related to external tetramethylsilane (δ = 0 ppm). For the catalytic studies, complexes **4** or **5**, respectively, and PPh_3 were mixed in NMR tubes in degassed, dry DMSO (0.6 mL) as solvent. The reactions were monitored by ^{31}P NMR spectroscopy. The presence of dimethyl sulfide in the reaction mixtures was detected by isolating Me_2S as $(Me_2S)(HgCl_2)_3$.[22] Elemental analyses were performed with an Elementar 4.1 vario EL 3 elemental analyzer. Infrared spectra were recorded as KBr pellets with a Digilab FTS 1000 from 4000 to 400 cm^{-1}. ESI-MS samples were disolved and recorded with an Applied Biosystems API 2000.

X-ray Structural Analysis: Diffraction data were collected at low temperature (–140.0 °C and –103.0 °C respectively) with a STOE-IPDS II or STOE-IPDS 2T diffractometer with graphite-monochromated molybdenum K_α radiation, λ = 0.71073 Å. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques (SHELXL-97).[23] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Compound **3** crystallizes as a merohedral twin and the respective twin-law was applied in the refinement. The crystal and refinement data are summarized in Table 1.

Table 1. Structure and refinement data for compounds **3** and **4′**.

	3	**4′**
Empirical formula	$C_8H_{10}O_2S_2$	$C_{20}H_{32}MoNa_2O_9S_4$
T /K	170(2)	133(2)
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a /Å	26.887(5)	8.3805(17)
b /Å	8.6731(17)	9.2807(19)
c /Å	20.875(4)	20.013(4)
α /°	90	101.83(3)
β /°	130.03(3)	97.32(3)
γ /°	90	100.05(3)
V /Å^3	3727.5 (13)	1478.4(5)
Z	16	2
$D_{calcd.}$ /g·cm^{-3}	1.442	1.542
μ /mm^{-1}	0.527	0.798
F(000)	1696	704
θ range /°	3.33 to 28.53	2.29 to 25.83
Data / restraints / parameters	4683 / 6 / 234	5633 / 0 / 346
Reflections collected / unique	9330 / 4683 (R_{int} = 0.0369)	11820 / 5633 (R_{int} = 0.0322)
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0459, 0.1098	0.0258, 0.0706
R_1, wR_2 (all data)[a]	0.0649, 0.1236	0.0281, 0.0707
GoF	1.022	1.079
$\Delta\rho$(max), $\Delta\rho$(min) /e·Å^{-3}	0.383, –0.478	0.650, –0.720

a) $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-922482 (**3**) and CCDC-922481 (**4′**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Molecular structure of 4,5-dimethoxybenzene-1,2-dithiolene (**3**).

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