Synthesis and Characterisation of a Dioxo-μ-Oxo Molybdenum Dimer: An Unusual case of a μ-Oxo Conformational Equilibrium

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A new thiocyanatomolybdenum(VI) dioxo-μ-oxo complex dimer bearing a 4,4′-di-*tert*-butyl-2,2′-bipyridine ligand (**2**) is shown to exist in the crystal cell unit as a meso (Mo-O–Mo angle of 180°) and d,l, pair (Mo–O–Mo angle of 155.7°). These conformers are in equilibrium in solution and have been observed clearly by ^{1}H NMR spectroscopy.

Introduction

Oxygenated complexes of transition metals are of utmost importance in catalytic oxidation processes. Among these complexes, metal-oxo species, found in a wide range of systems from metal-oxide surfaces to metalloenzymes, have received considerable attention.[1]

Two structural features describe the metal-oxo function: terminal-oxo (M=O) and bridging μ-oxo (M−O−M). Although most studies deal implicitly with the former type, binuclear oxo-metal entities have been shown to be key intermediates in many catalytic systems. For example, among the innumerable compounds known with μ-oxo ligands, ruthenium oxo-bridged complexes have already been shown to be active in the catalytic oxidation of water.[2] Later, high valent bimetallic μ-oxo species of Cu and Fe were found to take part in C−H bond activation.[3] Very recently some novel Co^{III} and Ni^{III} bis(μ-oxo) complexes have been isolated and characterized foreboding high oxidation capability.[4]

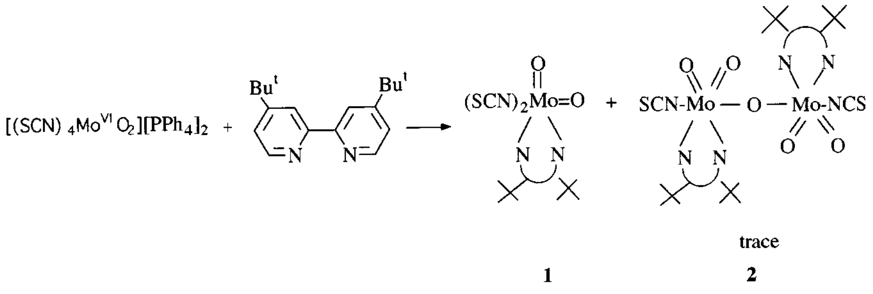
Polyoxometallates are well-defined anionic, oligomeric metal oxides featuring both terminal and bridging oxygen atoms. Among these, vanadium, molybdenum and tungsten anions are the most common and are often involved in oxidation reactions.[5]

This paper presents the synthesis and characterization of a molybdenum(VI) complex bearing both terminal and bridging oxo ligands which, in solution, exhibits a new μ-oxo conformational equilibrium which can be clearly observed by ^{1}H NMR spectroscopy.

Results and Discussion

In the course of a study of reactions of tetrathiocyanatodioxomolybdenum(VI) anions with substituted bipyridines,[6] a molybdenum(VI) dioxo complex (**1**) exhibiting exceptional oxidizing ability was obtained with the bulky 4,4′-di-*tert*-butyl-2,2′bipyridine (Scheme 1). This reaction was accompanied by the formation of traces of a μ-oxo dimer (**2**) thought to arise by an oxo-ligand redistribution process.

The remarkable properties of **1**[7] prompted us to develop a better method to synthesize compound **2** directly in order to test it also as a potential oxygen atom transfer agent. One plausible route consisted of replacing one thiocyanato group of **1** by a hydroxyl group, followed by dehydration. This reaction appeared to work but was not optimized. Instead a less cumbersome biphasic system was chosen starting directly from an aqueous solution of molybdate and thiocyanate, with the bipyridine in dichloromethane (Scheme 2).



Scheme 1

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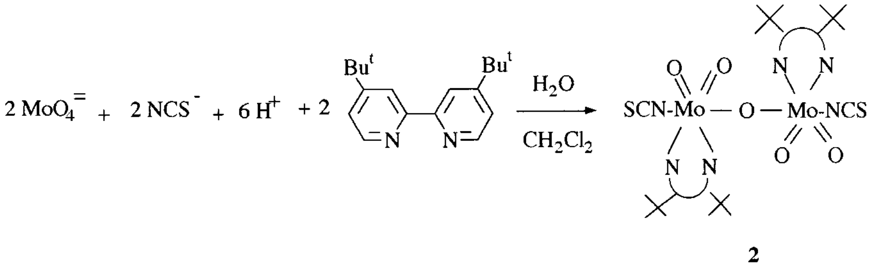

Scheme 2

The product was obtained as a light yellow crystalline solid exhibiting, in the IR spectrum, the characteristic bands for both terminal and μ-oxo functions, and those for the thiocyanato and the bipyridyl ligands.[8] An X-ray

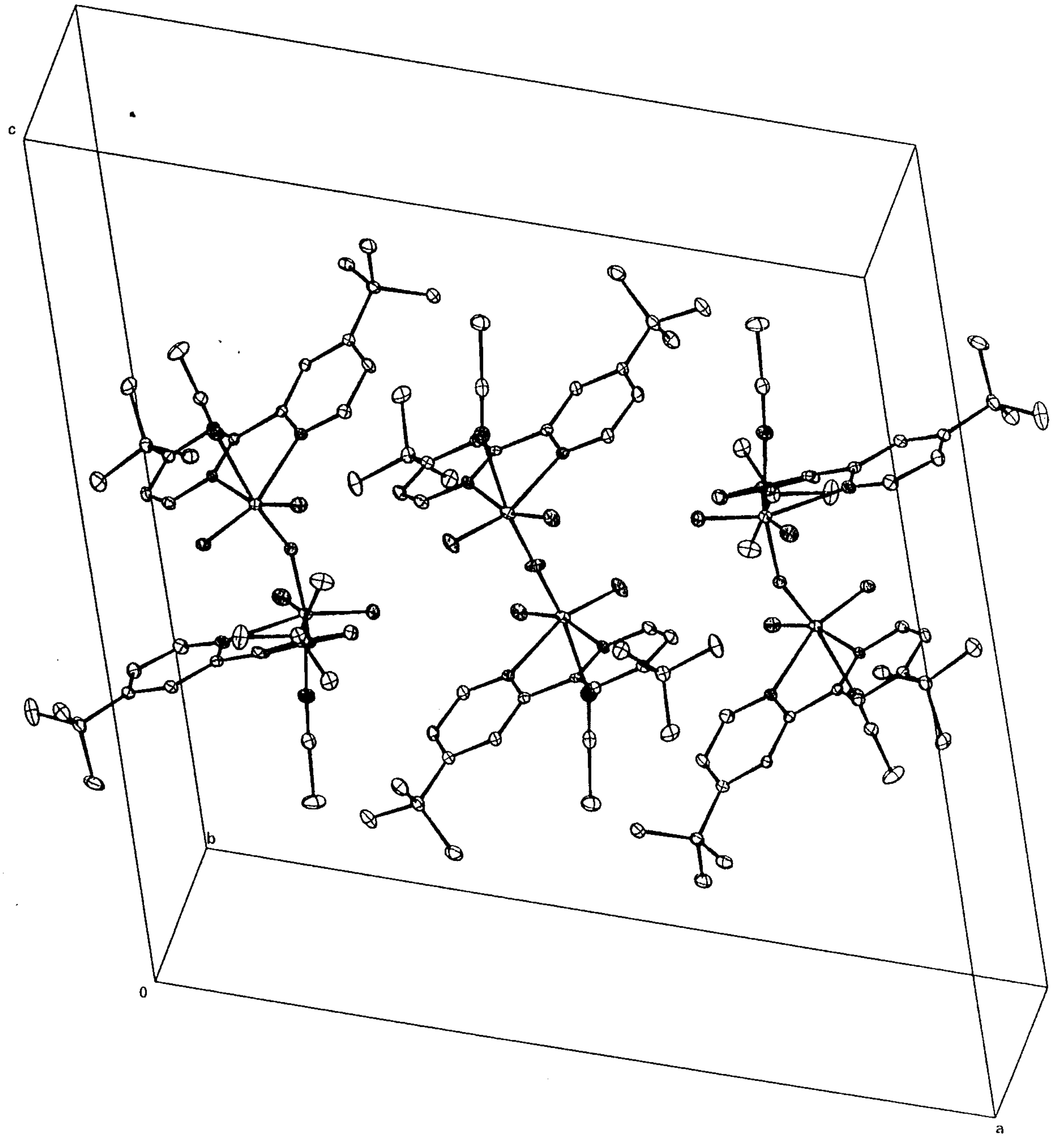

Figure 1. Unit cell of **2**

analysis of a suitable crystal confirmed these observations and, furthermore, uncovered an interesting feature – the cell unit was found to contain three molecules of **2** (see Figure 1), one with a Mo–O–Mo angle of 180°, with a center of symmetry located at the μ-oxo oxygen atom, and two others with a Mo–O–Mo angle of 155.7°, each totally unsymmetrical, with each of the four nitrogen-containing heterocycles in a different environment.

A closer examination reveals that these two molecules are enantiomers and, thus, the unit cell consists of a d,l, pair ($\mathbf{2}_{\mathrm{d,l,}}$) and a meso isomer ($\mathbf{2}_{\mathrm{meso}}$). Taken separately (see Figures 2 and 3) each molecule exhibits some interesting features; as expected, the two dioxo moieties are trans to each other in both the meso and the d,l conformers, however the thiocyanato ligands are slightly bent away from the molybdenum dioxo plane in the $\mathbf{2}_{\mathrm{meso}}$ conformer whereas they appear to be slightly bent towards the molybdenum dioxo plane in the case of the d,l pair $\mathbf{2}_{\mathrm{d,l}}$. The bipyridyl moiety is always coplanar with the molybdenum dioxo plane; however, all four nitrogen heterocycles are equivalent in the $\mathbf{2}_{\mathrm{meso}}$ conformer, whereas they are found in different environments in the $\mathbf{2}_{\mathrm{d,l}}$ conformer, with the consequence of having, in this case, four tertiary butyl groups also in a different environment. Finally the metal to oxygen bond lengths, either terminal or μ-oxo, have values similar to those reported for related compounds.[1a] Such a mixture of conformers in the solid state, although not unique, is quite scarce and could conceivably be rationalized by constraining stacking forces during crystallization.[9]

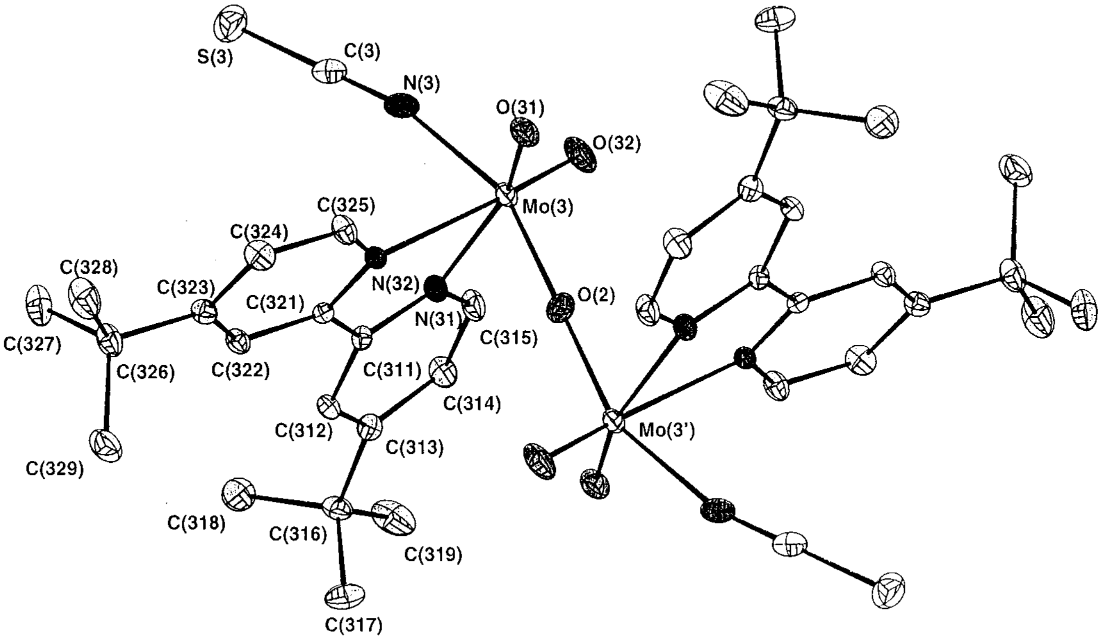

Figure 2. X-ray crystal structure of $\mathbf{2}_{\mathrm{meso}}$; selected bond lengths [Å] and angles [°]: Mo(3)–O(2) 1.876(1), Mo(3)–O(31) 1.694(2), Mo(3)–O(32) 1.701(2), Mo(3)–N(3) 2.112(3), Mo(3)–N(31) 2.317(3), Mo(3)–N(32) 2.307(2); Mo(3)–O(2)–Mo(3′) 179.99, N(31)–Mo(3)–N(32) 68.91(9), O(31)–Mo(3)–O(32) 106.3(1), O(31)–Mo(3)–N(32) 92.1(1), O(32)–Mo(3)–N(32) 158.7(1), O(2)–Mo(3)–N(31) 81.14(7), O(2)–Mo(3)–N(32) 84.65(6), O(2)–Mo(3)–N(3) 156.39(8), N(3)–Mo(3)–N(32) 75.6, O(32)–Mo(3)–N(3) 92.5(1)

Much more unexpected and unusual, however, was the ^{1}H NMR spectrum in solution. Contrary to the NMR spectrum of the monomeric dioxomolybdenum(VI) complex **1** which exhibits, as expected, the pattern for the bipyridyl moiety of three signals in the aromatic region and a singlet for the *tert*-butyl group, the spectrum of **2** ($CDCl_3$ 25°C) showed five well-separated ”sets” of bipyridyl signals. One integrating for 44% and the other four, of equal intensity, integrating for a total of 56% (Figure 4).

The presence of five anisotropically different tertiary butyl groups was also observed; one major signal integrating for 44% and four others, of equal intensity, integrating jointly for 56%. The interpretation of such spectra can only be done in terms of an unprecedented μ-oxo conformational equilibrium between the $\mathbf{2}_{\mathrm{meso}}$ conformer, with four equal pyridyl rings (44%), and the $\mathbf{2}_{\mathrm{d,l}}$ conformer, with four distinct pyridyl rings resonating at different fields due to their anisotropically different environment (56%). The presence of such an equilibrium was confirmed in various ways. First, changing the NMR solvent from $CDCl_3$ to CD_2Cl_2 resulted in a slightly, but significantly, different ratio of conformers ($\mathbf{2}_{\mathrm{meso}}/\mathbf{2}_{\mathrm{d,l}}$ = 44:56 in $CDCl_3$ and 55:45 in CD_2Cl_2). Second, a variable temperature NMR spectroscopic analysis added supporting evidence: upon lowering the temperature (from 25°C to −60°C) the signals sharpened, but the $\mathbf{2}_{\mathrm{meso}}/\mathbf{2}_{\mathrm{d,l}}$ ratio varied only very slightly (44:55 at 25°C vs 40:60 at −60°C). This is not unexpected for a conformeric mixture close to 50:50. However, upon increasing the temperature (from 25°C to 130°C), the signals corresponding to the four distinct pyridyl ring hydrogens of the $\mathbf{2}_{\mathrm{d,l}}$ conformer quickly broaden, collapse and then slowly coalesce with the signals of $\mathbf{2}_{\mathrm{meso}}$. The energy barrier estimated from this analysis is about 75 kJ·mol^{-1}. It is noteworthy that upon cooling the solution back to 25°C the original spectrum was obtained thus indicating the presence

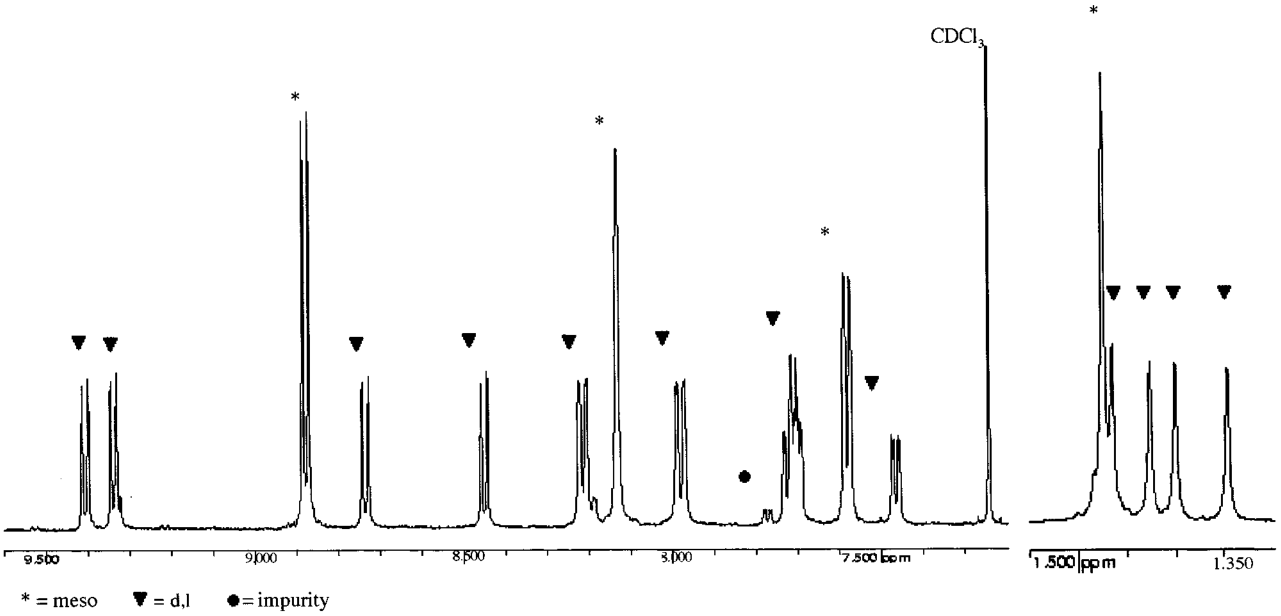

Figure 4. ^{1}H NMR spectrum of **2** (400 MHz, CDCl$_3$, −50°C)

of an equilibrium. The ^{95}Mo NMR spectrum also supports the presence of two distinct species in solution; it exhibits two resonances at −45 and −57 ppm. The relatively small difference between these two signals indicates that the electronic density at the metallic center is very slightly perturbed in going from one conformer to the other, es-

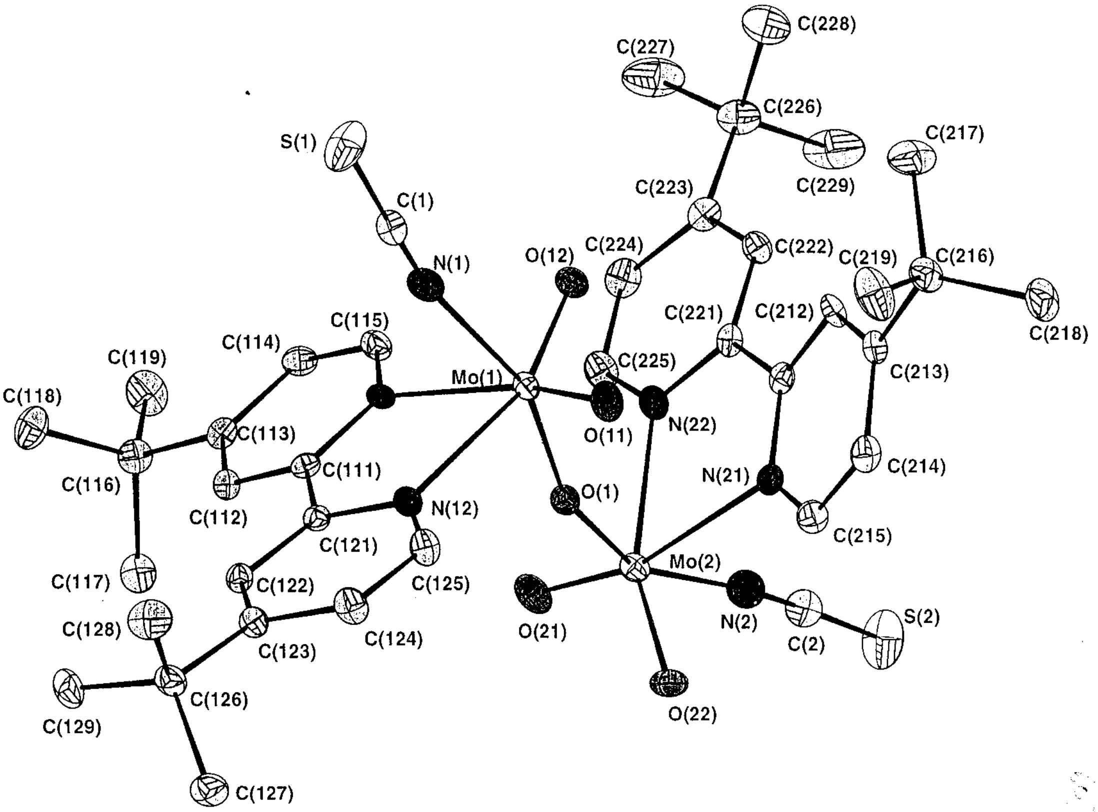

Figure 3. X-ray crystal structure of $\mathbf{2}_{d,l}$; selected bond lengths [Å] and angles [°]: Mo(1)−O(1) 1.892(2), Mo(2)−O(1) 1.895(2), Mo(1)−O(11) 1.696(2), Mo(2)−O(21) 1.690(2), Mo(1)−O(12) 1.700(2), Mo(2)−O(22) 1.703(2), Mo(1)−N(1) 2.139(3), Mo(2)−N(2) 2.098(3), Mo(1)−N(11), 2.313(3), Mo(2)−N(21) 2.329(3); Mo(1)−O(1)−Mo(2) 155.7(1), O(11)−Mo(1)−N(1) 92.0(1), O(21)−Mo(2)−N(2) 94.1(1), O(1)−Mo(1)−N(11) 80.59(9), O(1)−Mo(2)−N(21) 78.13(9), N(1)−Mo(1)−N(11) 80.9(1), N(2)−Mo(2)−N(21) 82.6(1), O(1)−Mo(2)−N(22) 84.53(9), 86.67(9), Mo(1)−N(1)−C(1) 164.2(3), Mo(2)−N(2)−C(2) 174.2(3), Mo(1)−N(11)−C(111) 120.4, Mo(2)−N(21)−C(211) 117.6

pecially if one compares the value of + 63 ppm for compound **1**.[6]

Although the interconversion between $\mathbf{2}_{meso}$ and $\mathbf{2}_{d,l}$ can easily be described, based on molecular models, by a bending of the Mo−O−Mo bond accompanied by a slight tilting of the bipyridyl moiety, the real reason for the existence of *two* stable conformers remains unclear. Studies are in progress to establish which oxygen atom in **2** is most prone to be transferred to a substrate. The dynamics of this μ-oxo conformational equilibrium, although never directly observed before, could be implied in numerous isomerisation processes of oxometallate anions and, in turn, give a better insight to the more general oxygen atom transfer reactions.

Experimental Section

Synthesis of 2: To an aqueous solution (30 mL) containing Na_2MoO_4 (0.50 g, 2.4 mmol) and KSCN (0.92 g, 9.6 mmol) was slowly added 9.6 mL of 1N HCl (9.6 mmol). The resulting yellow solution was stirred for 15 min followed by the addition of a CH_2Cl_2 solution (60 mL) containing 4,4′-di-*tert*-butyl-2,2′-bipyridine (0.64 g, 2.4 mmol). Vigorous stirring for an additional 30 min resulted in a yellow organic layer which was separated, dried and evaporated to give **2** (0.95 g, 76%) as a yellow solid. Recrystallization (−15°C) from CH_2Cl_2/*n*-hexane (2:1) afforded light yellow needles (m.p. > 180°C). − IR(KBr): $\tilde{\nu}$ = 2065 (-NCS), 940, 905 (= O), 775 (-O-) cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$, 21°C, TMS): δ = 1.36 (s), 1.41 (s), 1.43 (s), 1.48 (s), 7.45 [d, *J*(H-H) = 6 Hz], 7.57 [dd, *J*(H-H) = 6 Hz, 1.6 Hz], 7.69 [t, *J*(H-H) = 6 Hz], 7.98 [d, *J*(H-H) = 6 Hz], 8.14[d, *J*(H-H) = 1.6 Hz], 8.24[d, *J*(H-H) = 6 Hz], 8.51[d, *J*(H-H) = 6 Hz], 8.78 [d, *J*(H-H) = 6 Hz], 8.89 [d, *J*(H-H) = 6 Hz], 9.36 [d, *J*(H-H) = 6 Hz], 9.406 [d, *J*(H-H) = 6 Hz]. − ^{13}C NMR (101MHz, $CDCl_3$, 21°C, TMS): δ = 30.2, 30.3, 35.8, 118.6, 118.8, 119.1, 123.7, 124.1, 124.3, 124.5, 148.9, 149.7, 150.0, 150.5, 151.0, 151.7, 152.8, 165.4, 165.7. − ^{95}Mo NMR (26MHz, $CDCl_3$, 21°C, Na_2MoO_4, pH = 11): δ = −45, −57. − $C_{38}H_{48}Mo_2N_6O_5S_2$ (924): calcd. C 49.35, H 5.23, N 9.09; found C 49.35, H 5.15, N 9.23.

X-ray Crystal Structure Analysis of 2: $C_{28}H_{72}Mo_3N_9O_7$.5S3·CH2Cl2 (M_r = 1472.2); needle (0.44 × 0.12 × 0.12 mm); monoclinic, space group $P2_1/c$; a = 21.407(3), b = 15.054(2), c = 21.512(3)Å, β = 106.94(1)°, V = 6631(1)$Å^3$, Z = 4, F(000) = 2992, ρ_{calcd} = 1.475Mg/m^3, μ(Mo-K_α) = 7.708cm^{-1}; IPDS Stoe diffractometer, graphite monochromator, Mo-K_α radiation (λ = 0.71073), detector distance = 80 mm, ø scan (0 < ø < 250 deg), 3.9 < 2Θ < 48.7°, numerical (X-SHAPE) absorption method,[10] number of reflexions collected = 52657, number of unique reflexions = 10360, merging factor R(int) = 0.0543, reflexions used ($I_0 > 1\sigma(I_0)$) = 6188, R = 0.0288, R_w = 0.0313, Chebyschev weighting scheme,[11] GOF = 1.088, 746 variable parameters. The structure was solved by direct methods (SIR 92)[12] and refined with least-squares procedures on Fobs. The calculations were carried out with a CRYSTALS package program.[13] The drawing was realized with CAMERON[14] and the atomic scattering factors were taken from International Tables.[15] Crystallographic data (excluding structure factors) for the structure reported above have been deposited at the Cambridge Crystallographical Data Centre as supplementary publication no.CCDC 113727. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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