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Molybdenum Complexes Bearing the Tris(1-pyrazolyl)methanesulfonate Ligand: Synthesis, Characterization and Electrochemical Behaviour

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The tris(1-pyrazolyl)methanesulfonate lithium salt Li(Tpms) [Tpms = $SO_3C(pz)_3^-$] reacts with $[Mo(CO)_6]$ in NCMe heated at reflux to yield $Li[Mo(Tpms)(CO)_3]$ (**1**), which, upon crystallization from thf, forms the coordination polymer $[Mo(Tpms)(CO)_2(\mu\text{-}CO)Li(thf)_2]_n$ (**2**). Reaction of **1** with I_2, HBF_4 or $AgBF_4$ yields $[Mo(Tpms)I(CO)_3]$ (**3**), $[Mo(Tpms)H(CO)_3]$ (**5**) or $[Mo(Tpms)O_2]_2(\mu\text{-}O)$ (**7**), respectively. The high-oxidation-state dinuclear complexes $[\{Mo(Tpms)O(\mu\text{-}O)\}_2]$ (**4**) and $[\{Mo(tpms)OCl\}_2](\mu\text{-}O)$ (**6**) are formed upon exposure to air of solutions of **3** and **5**, respectively. Compounds **1**–**7**, which appear to be the first tris(pyrazolyl)methanesulfonate complexes of molybdenum to be reported, were characterized by IR, ^1H and ^{13}C NMR spectroscopy, ESI-MS, elemental analysis, cyclic voltammetry and, in the cases of Li(Tpms) and compounds **2**, **4**·$2CH_3CN$, **6**·$6CHCl_3$ and **7**, by X-ray diffraction analyses. Li(Tpms) forms a 1D polymeric structure {i.e., $[Li(tpms)]_n$} with Tpms as a tetradentate N_2O_2 chelating ligand that bridges two Li cations with distorted tetrahedral coordination. Compound **2** is a 1D coordination polymer in which Tpms acts as a bridging tetradentate N_3O ligand and each $Li(thf)_2^+$ moiety is coordinated by one bridging CO ligand and by the sulfonyl group of a contiguous monomeric unit. In **4**, **6** and **7**, the Tpms ligand is a tridentate chelator either in the NNO (in **4**) or in the NNN (in **6** and **7**) fashion. Complexes **1**, **3** and **5** exhibit, by cyclic voltammetry, a single-electron oxidation at oxidation potential values that indicate that the Tpms ligand has an electron-donor character weaker than that of cyclopentadienyl.

Introduction

Facially coordinating tridentate nitrogen donor ligands have experienced a rapid development over the years, and tris(pyrazolyl)borates in particular constitute a highly successful type of ligand, as they form complexes with applications in various fields such as catalysis, metal extraction and bioinorganic modelling.[1–11] Their success results largely from the ability to tune steric[1,12] and electronic[12,13] properties. Since Trofimenko synthesized the poly(1-pyrazolyl)-borate ligands,[14,15] they have experienced a growing number of applications and have become the most commonly used tripodal ligands.[1,2–24] However, they have the disadvantage of being insoluble in water and unstable towards hydrolysis.[1,10] To obtain complexes that are soluble and stable under physiological conditions and that could therefore be used as better enzyme models, Kläui and co-workers reported[25] the synthesis of the novel tris(1-pyrazolyl)methanesulfonate (Tpms) ligand that relates to the conventional hydrotris(1-pyrazolyl)borate (Tp) species (Figure 1). Both can act as monoanionic, C_{3v}-symmetrical N-donor ligands, but instead of the boron hydride unit of Tp, Tpms bears a methanesulfonate group, which affords good stability towards hydrolysis and increased solubility in polar solvents (e.g., water and methanol).

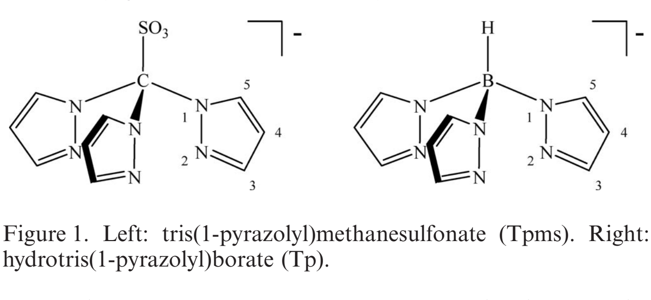

Figure 1. Left: tris(1-pyrazolyl)methanesulfonate (Tpms). Right: hydrotris(1-pyrazolyl)borate (Tp).

In spite of these useful features, the coordination chemistry of Tpms remains little explored. Hence, also in view of our interest toward the synthesis of Tpms complexes with diverse transition metals, namely, V,[26] Re,[27] Fe[26] or Cu,[26,28] and their application in catalysis,[26,29–31] and in pursuit of our long-standing studies on the chemistry of

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molybdenum,[32,33] we decided to investigate the unexplored Tpms–Mo coordination chemistry. The main goals of the current study are as follows: (i) extend the promising coordination chemistry of Tpms to Mo; (ii) investigate the structural role of the sulfonate group in the resulting complexes; and (iii) compare the geometrical and electronic properties of the Tpms–Mo complexes with those of the Tp analogues.

Several Mo complexes with the neutral unfunctionalized hydrotris(1-pyrazolyl)methane Tpm [Tpm = $HC(pz)_3$] and its substituted derivatives are known.[5,6] The first one, $[Mo(Tpm)(CO)_3]$, has been obtained from the reaction of $[Mo(CO)_6]$ with Tpm[34] and shown to be a versatile starting material. Several mononuclear and binuclear molybdenum compounds with the methyl-substituted $[HC(3,5\text{-}Me_2pz)_3]$ ligand were also reported.[35] The oxidation of $[\{HC(3,5\text{-}Me_2pz)_3\}Mo(CO)_3]$ by various oxidants, such as $SOCl_2$, Br_2, I_2 and HNO_3, was described, ultimately affording mononuclear Mo^{III} and Mo^{VI} complexes of the type $[\{HC(3,5\text{-}Me_2pz)_3\}MoX_3]$ (X = Cl, Br, I and O).[35] Dimolybdenum complexes that possess the thermodynamically stable $(Mo_2O_4)^{2+}$ core were also obtained.[35]

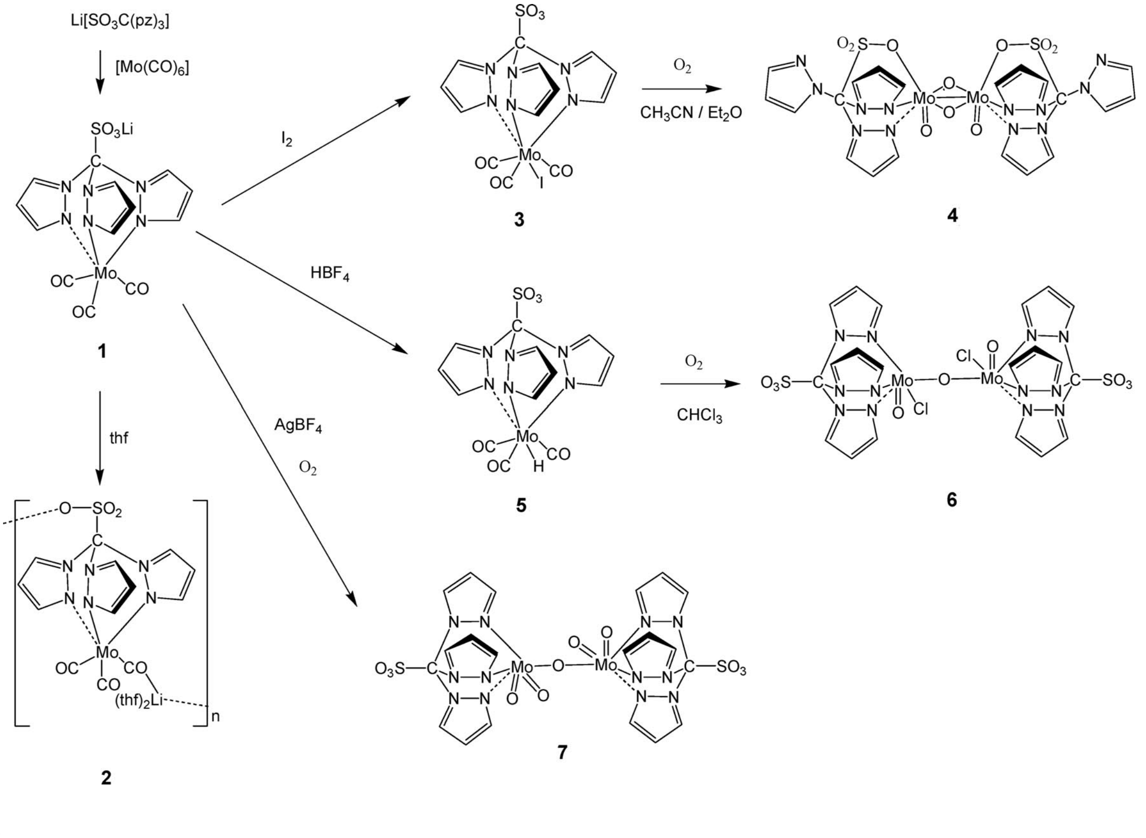
More recently, the syntheses of the molybdenum(0) $[Mo(CO)_3(\mathbf{L}_3)]$, $[Mo(CO)_4(\mathbf{L}_2)]$, $[Mo(CO)_3(NCMe)(\mathbf{L}_2)]$ and molybdenum(VI) $[MoCl_2O_2(\mathbf{L}_2)]$ complexes were performed with the tridentate ($\mathbf{L}_3$) and bidentate ($\mathbf{L}_2$) poly(pyrazolyl)methane ligands (G*n*-*dend*)$OCH_2C(pz)_3$ ($\mathbf{L}_3$) and (G*n*-*dend*)$CH(3,5\text{-}Me_2pz)_2$ ($\mathbf{L}_2$) [G*n*-*dend* = poly(benzyl ether) dendron].[36] Reactions of $[MoO_2Cl_2(thf)_2]$ with potential mono- and bidentate pyrazole-type ligands lead to octahedral complexes of formula $[MoO_2Cl_2(\mathbf{L}_1)_2]$ and $[MoO_2Cl_2(\mathbf{L}_2)]$ ($\mathbf{L}_1$ = 3,5-Me_2pz; $\mathbf{L}_2$ = $Me_2C(pz)_2$),[36] whereas reactions of $[MoO_2X_2(thf)_2]$ (X = Cl or Br) with potential tridentate ligands (e.g., tris(pyrazolyl)methane or tris(pyrazolyl)borate) lead to the replacement of both coordinated solvent molecules and one of the halogen ligands to give $[MoO_2X(\mathbf{L}_3)]X$ [X = Cl or Br, $\mathbf{L}_3$ = $HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$].[36] These complexes were shown to catalyze cyclooctene epoxidation with *t*BuOOH.[37] In addition, oxidation of $[Mo(Tpm)(CO)_3]$ by I_2 or Br_2 gave rise to the seven-coordinate $[Mo(Tpm)X(CO)_3]X$ derivatives (X = I or Br), whereas protonation with HBF_4 afforded the hydrido complex $[Mo(Tpm)H(CO)_3][BF_4]$.[38]

In contrast to the above-described Tpm Mo derivatives, the reactivity with Mo of the related anionic sulfonate-functionalized species [i.e., the tris(1-pyrazolyl)methanesulfonate (Tpms)], had not yet been investigated, to the best of our knowledge. This has encouraged us, within the above goals of the present study, to prepare the first Mo–Tpms compounds, to examine their properties and, when appropriate, to compare them with those of the neutral Tpm analogues.

Results and Discussion

Synthesis and Characterization of $Li[Mo(Tpms)(CO)_3]$ (1) and Its Conversion to $[Mo(Tpms)(CO)_2(\mu\text{-}CO)Li(thf)_2]_n$ (2)

Reaction of the lithium salt Li(Tpms) [Tpms = $SO_3C(pz)_3$] with $[Mo(CO)_6]$ in CH_3CN heated at reflux afforded $Li[Mo(Tpms)(CO)_3]$ (**1**), isolated in high yield as a yellow-



Scheme 1.

ish-green powder upon concentration of the reaction solution (Scheme 1). Compound **1** is air-sensitive, particularly in solution, and is readily soluble in water ($S_{25\,°C} \approx 16\,\mathrm{mg\,mL^{-1}}$) and in other polar solvents such as MeOH, CH_3CN, thf, $CHCl_3$ and CH_2Cl_2. The ^1H and ^{13}C NMR spectra of **1** in CD_3OD are indicative of a C_{3v} symmetry, with the Tpms ligand coordinated to the Mo atom through the three equivalent pyrazolyl groups. Its solid-state infrared spectrum shows strong ν(CO) bands at 1916 and 1756 (broad) cm^{-1}. These values are considerably lower than those for $[Mo(CO)_6]$, 1990 cm^{-1},[39] which is consistent with a greater extent of Mo–CO π backbonding in the $[Mo(Tpms)(CO)_3]^-$ unit than in the hexacarbonylmolybdenum compound. The Tpms ligand, in fact, replaces three stronger π-acceptor carbonyl groups in $[Mo(CO)_6]$, thereby increasing the metal-electron density. A comparison with $[Mo(Tp)(CO)_3]^-$ and $[Mo(Cp)(CO)_3]^-$ (Cp = η^5-C_5H_5), the hydrotris(1-pyrazolyl)borate and cyclopentadienyl analogues, respectively, reveals that the CO IR frequencies decrease in the order Tpms > Cp > Tp (e.g., 1900, 1796, 1747 cm^{-1} for $[Mo(Cp)(CO)_3]^-$,[40] and 1890, 1750 cm^{-1} for $[Mo(Tp)(CO)_3]^-$),[41] thus suggesting the opposite order of the electron-donor character of those ligands (i.e., Tp > Cp > Tpms).

The electrospray ionisation (ESI) MS spectrum of compound **1** in CH_3CN (Figure S1 in the Supporting Information), in the negative mode, shows a very clean isotopic pattern centred at m/z = 475, which agrees with the theoretical isotopic distribution of $[Mo(Tpms)(CO)_3]^-$. The same pattern is also observed in CH_2Cl_2.

Recrystallization from hot CH_3CN of Li(Tpms) afforded white crystals that were analyzed by X-ray diffraction (Figure 2). Each $[Tpms]^-$ unit bridges two Li cations that act as a bidentate N,O ligand for each of them and, on the whole, as a tetradentate N_2O_2 chelating agent. The 1D polymeric structure that is formed shows a zigzag arrangement in which three different atom chains can be outlined (Figure S2 in the Supporting Information): –(Li–O–S–O)–, –(Li–N–N–C–S–O)– and –(Li–N–N–C–N–N)–. The metal centres present distorted tetrahedral environments, each one joining two six–membered Li–O–S–C–N–N cycles in a spirobicyclic fashion. As a consequence of the severe strain conferred by these cycles, the internal O–Li–N bond angles are considerably smaller [92.2(8)–96.7(8)° range] than the other four angles [104.5(9)–126.4(12)° range]. The highest values of the O–Li–N angles involve different Tpms ligands.

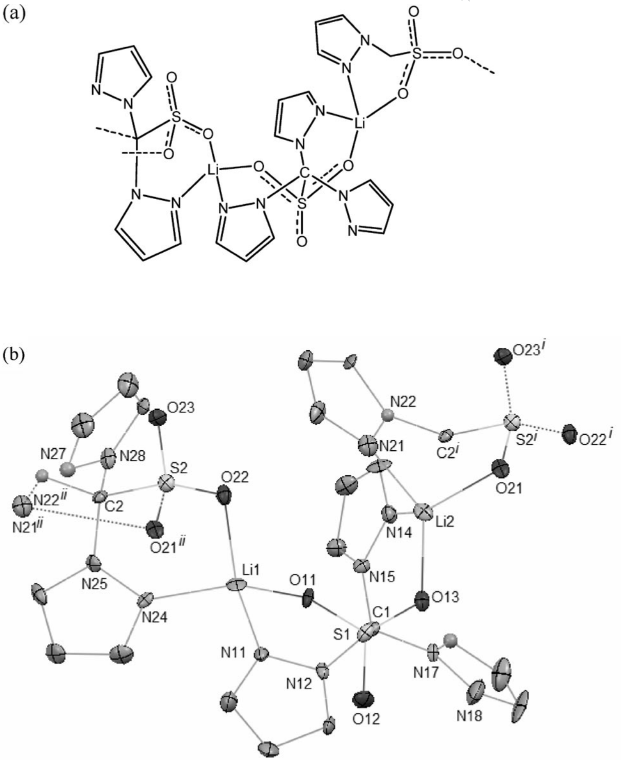


Figure 2. (a) Fragment of $[Li(Tpms)]_n$ and (b) ORTEP arbitrary view with atom labelling scheme. Thermal ellipsoids are drawn at 30% probability. All hydrogen atoms were omitted for clarity. Selected distances [Å]: Li1–N11 2.015(19), Li1–N24 2.02(2), Li1–O11 1.93(2), Li1–O22 1.94(2), Li2–N14 2.06(2), Li2–N21 2.062(19), Li2–O13 1.891(19), Li2–O21 1.93(2), S1–O11 1.455(7), S1–O12 1.424(12), S1–O13 1.454(8), S2–O21 1.444(8), S2–O22 1.455(8), S2–O23 1.449(12). Selected angles [°]: O11–Li1–O22 112.3(11), N11–Li1–N24 107.1(10), O11–Li1–N11 94.6(9), O22–Li1–N24 94.9(9), O22–Li1–N11 126.4(12), O11–Li1–N24 124.4(12), O13–Li2–O21 116.2(11), N21–Li2–N14 104.5(9), O13–Li2–N14 96.7(8), O21–Li2–N21 92.2(8), O13–Li2–N21 126.0(9), O21–Li2–N14 123.5(9). Symmetry codes to generate equivalent atoms: *i*: x, $1 + y$, z; *ii*: x, $-1 + y$, z.

Upon recrystallization of **1** from thf/Et_2O at 0 °C, green crystals of the new compound $[Mo(Tpms)(CO)_2(\mu\text{-}CO)Li(thf)_2]_n$ (**2**) were obtained and analyzed by X-ray diffraction (Figure 3, Scheme 1). Compound **2** is a 1D-type coordination polymer in which the $[Mo(Tpms)(CO)_3]^-$ moiety acts as a building block that leads to an asymmetric unit containing one Mo centre and one $Li(thf)_2$ moiety bound to the O12 atom of the sulfonyl group and to the O3 atom of a bridging CO (Figure 3). The Tpms group acts as a bridging tetradentate ligand in the N,N,N,O (κ^4:*N*,*N*,*N*,*O*) coordination mode, bound to the Mo atom through the pyrazolyl nitrogen atoms N11, N14 and N17, and to the Li atom through the O12 oxygen atom. The N–Mo–N angles are restrained by this chelating ligand and range from 77.29(16) to 77.79(16)°; the wider C–Mo–X (X = C or N) angle ranges from 86.3(2) to 175.0(2)°, therefore leading to a highly distorted octahedron around the Mo atom. The Mo–N–N–C torsion angles of the pyrazolyl rings display values from 174.90 to 177.75°, thus revealing a low degree of tilting of the rings. The O_4 environment around the Li^+ cation shapes an almost regular tetrahedron (O–Li–O angles in the 108.1(5)–114.4(5)° range). The solid-state structure of compound **2** also exhibits the presence of intermolecular C–H···π interactions (Figure S2 in the Supporting Information) between the thf C202–H20D and the N17–N18 pirazolyl ring (H···centroid distance of 2.777 Å with a C–H···centroid angle of 145.23°), as well as (although considerably weaker) between the C202–H20C and the N11–N12 pyrazolyl ring (H···centroid distance of 3.061 Å with a C–H···centroid angle of 139.34°). These interactions, together with several hydrogen bonds that involve all the oxygen atoms, help to stabilize the structure in the solid state. Structure **2** can be qualified as a heterometallic supramolecular chain. The nearest distance between two Mo atoms or two Li atoms in a chain is 10.794 Å, the same as the unit cell parameter *b*. The shortest interchain Mo···Mo, Li···Li and Mo···Li distances are 7.196, 9.734 and 7.462 Å, respectively. These distances considerably exceed the sum of the van der Waals radii of two Mo or two Li atoms and hence the chains are effectively separated, as shown in Figures S3 and S4 in the Supporting Information.

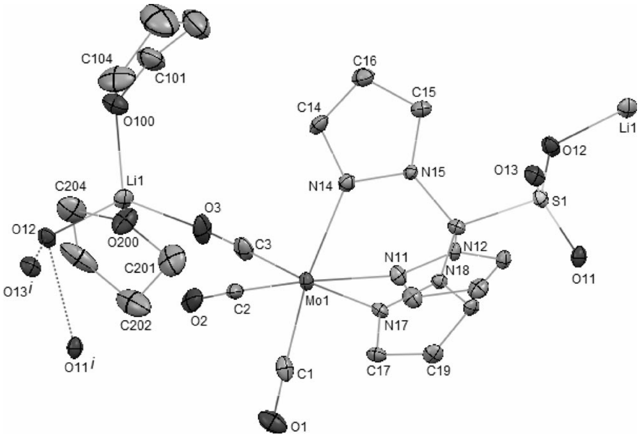
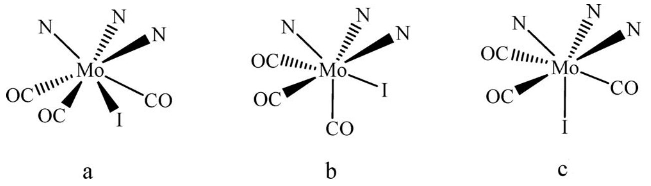


Figure 3. ORTEP view of the asymmetric unit of $[Mo(Tpms)(CO)_2(\mu\text{-}CO)Li(thf)_2]_n$ (**2**) with atom labelling scheme. Thermal ellipsoids are drawn at 30% probability. All hydrogen atoms were omitted for clarity. Selected distances [Å]: Mo1–N11 2.226(4), Mo1–N14 2.245(5), Mo1–N17 2.232(4), Mo1–C1 1.922(7), Mo1–C2 1.911(6), C1–O1 1.174(7), C2–O2 1.159(6), C3–O3 1.194(7), O3–Li1 1.898(10), O12–Li1^i 1.933(10), Li1–O100 1.929(10), Li1–O200 1.894(11), S1–O11 1.432(4), S1–O12 1.451(4), S1–O13 1.433(4). Selected angles [°]: N11–Mo1–N14 77.29(16), N11–Mo1–N17 77.47(16), N17–Mo1–N14 77.79(16), C3–Mo1–N17 175.0(2), C3–Mo1–C2 86.5(2), O1–C1–Mo1 178.8(5), O2–C2–Mo1 177.1(5), O3–C3–Mo1 177.0(5), C3–O3–Li 164.9(5). Symmetry codes to generate equivalent atoms: *i*: *x*, –1 + *y*, *z*.

Reactions of $Li[Mo(Tpms)(CO)_3]$ (1) with I_2

The controlled oxidation of complex **1** with iodine (1 equiv.) gave a reddish-brown product formulated as $[Mo(Tpms)I(CO)_3]$ (**3**) on the basis of IR, ^1H NMR and ^{13}C NMR spectroscopy. Complex **3** is diamagnetic, air sensitive and readily soluble in chlorinated hydrocarbons, CH_3CN, thf and also in water ($S_{25\,°C} \approx 5$ mg mL^{-1}), and not considerably soluble in alcohols, diethyl ether and hydrocarbon solvents. In accordance with a C_s symmetry, the infrared spectrum of **3** in the solid state shows three carbonyl stretching bands (2A′ + A′′) at 2039, 1966 and 1944 cm^{-1}. They are shifted to higher frequencies than those of the starting Mo^0 tricarbonyl complex, thus reflecting the decrease in electron density at the central metal atom as a result of the oxidation. This pattern is consistent with either a 4:3 "piano stool" structure[38,41] or a 3:3:1 structure with axial CO[39] (Scheme 2a and b, respectively). Both these possibilities have already been reported for related complexes, such as $[Mo(Tp)Br(CO)_3]$[41] and $[Mo(Tpm)Br(CO)_3]$[38] (4:3 "piano stool" structure) or $[Mo(Tp\textit{i}Pr)I(CO)_3]$[42] (3:3:1 carbonyl-capped octahedral structure). The 3:3:1 structure with the halide in the axial position (Scheme 2c) has never been observed and is excluded by the IR study because its C_{3v} symmetry would require only two normal stretching modes (A_1 + E) for the carbonyl groups.



Scheme 2. Possible isomers for the seven-coordinate complex **3**. **a**: 4:3 "piano stool" structure (C_s symmetry). **b**: 3:3:1 structure with CO in the axial position (C_s symmetry). **c**: 3:3:1 structure with I in the axial position (C_{3v} symmetry).

A comparison with the hydrotris(1-pyrazolyl)borate analogue $[Mo(Tp)I(CO)_3]$ reveals that the Tpms complex exhibits *ν*(CO) frequencies higher than those of the latter compound (2016, 1950, 1910 cm^{-1}),[41] also in accordance with the lower electron-donor character of Tpms relative to Tp.

The ^1H NMR analysis of complex **3** shows one set of equivalent pyrazolyl rings, therefore indicating a fluxional process on the NMR spectroscopy timescale. The fluxionality of seven-coordinate molybdenum(II) and tungsten(II) complexes is well known.[38,41–43]

Slow diffusion of Et_2O into a saturated solution of complex **3** in CH_3CN afforded reddish-brown crystals suitable for X-ray diffraction study. The data revealed the tetraoxo Mo^V dimer $[\{Mo(Tpms)O(\mu\text{-}O)\}_2]$ (**4**) (Scheme 1 and Figure 4), which crystallized with two molecules of CH_3CN. Compound **4** derived from the slow oxidation of **3** with air, as a consequence of O_2 diffusion during the crystallization procedure.

The asymmetric unit of **4** comprises half of the complex molecule and one CH_3CN molecule. The binuclear complex contains a crystallographically imposed twofold axis that passes through the centre of the Mo1–Mo1^i bond, perpendicularly to the central Mo_2O_2 plane. The molecular geometry is that of a typical edge-sharing bioctahedron, with two terminal oxo ligands placed on the same side (*syn*) of the Mo_2O_2 place, and two bridging O atoms, thus displaying the well-known $(Mo_2O_4)^{2+}$ bridging structure found in many compounds.[44,45–48] The anionic Tpms group acts as a tridentate N,N,O ligand. The basal positions in each octahedron are occupied by the N11 and N14 atoms and the bridging O2 oxygen atoms and the two distorted octahedra share the common O2–O2^i edge; the apical positions are taken up by the oxido O1 and O12 atoms from the sulfonate group. Due to the sulfonate coordination, the S1–O12 bond length of 1.472(2) Å is slightly longer than the other two S1–O distances [1.435(2) and 1.438(2) Å]. The Mo–Mo distance is 2.5545(4) Å, similar to that in related Mo^V dinuclear compounds,[46,48,49] and is consistent with a metal–metal single bond. The disparity in the terminal and bridging molybdenum–oxygen distances (Figure 4) is also found in other Mo_2O_4 structures.[49] The O2–Mo1–N14^i

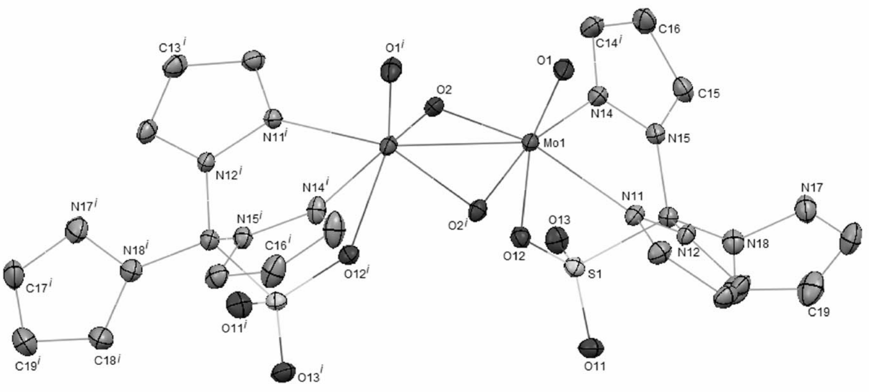


Figure 4. An ORTEP view of compound [Mo(Tpms)O(μ-O)]$_2$·2CH$_3$CN (**4**·2CH$_3$CN). The CH$_3$CN molecules and the hydrogen atoms are omitted for clarity. Selected distances [Å]: Mo1–N11 2.189(2), Mo1–N14 2.211(2), Mo1–O1 1.673(2), Mo1^{i}–O2 1.9345(18), Mo1–O2 1.940(2), Mo1–O12 2.303(2), Mo1–Mo1^{i} 2.5545(4), S1–O11 1.435(2), S1–O12 1.472(2), S1–O13 1.438(2). Selected angles [°]: N11–Mo1–N14 82.47(9), O12–Mo1–N14 75.80(8), O1–Mo1–O12 162.95(9), Mo1–O2–Mo1^{i} 82.50(7), O2–Mo1–O2 94.25(8), O2–Mo1–Mo1^{i} 48.66(5). Symmetry code to generate equivalent atoms *i*: 1 – *x*, *y*, 3/2 – *z*.

[163.61(9)°] and O2–Mo1–N11^{i} [156.12(9)°] angles in the equatorial plane, together with the O12–Mo1–O1 [162.95(9)°] angle in the axial plane, are rather compressed and force the Mo1 and the bridging O2 oxygen atoms to shift away, in opposite directions, from the least-square basal plane. As a consequence, the Mo–O2–Mo^{i} and the Mo–O2^{i}–Mo^{i} planes make an angle of 25.83°. A similar folding has already been reported for other related structures (149° in [{Mo(Cp*)O$_2$}$_2$] (Cp* = η^5-C$_5$Me$_5$)[50] and 152° in [{Mo(Cp)O$_2$}$_2$][51]) and was shown to allow the formation of the Mo–Mo bond without excessively distorting the Mo–O–Mo angles in the bridge, which usually take values very close to the 82.50(7)° angle found in our case (83.3° in [{Mo(Cp*)O$_2$}$_2$][50] and 84.2° in [{Mo(Cp)O$_2$}$_2$][51]).

The structure of **4** is further stabilized by weak hydrogen bonds [shortest *d*(D···A) 3.158(5) Å; shortest angle (DHA) 133.00°] that involved the noncoordinated O11 atom of the sulfonate group, which simultaneously interacts with one of the pyrazolyl groups of a vicinal dimer and with the methyl group of a CH$_3$CN molecule, the nitrogen atom of which, in turn, interacts with a pyrazolyl ring of a third molecule. No specific π···π stacking interactions are identifiable between the pyrazolyl rings, the shortest interaction between the N14-containing pyrazolyl rings of neighbouring molecules being 4.360 Å.

Reactions of Li[Mo(Tpms)(CO)$_3$] (1) with HBF$_4$

Complex **1** is readily protonated with HBF$_4$ in dry acetonitrile to give the hydrido species [Mo(Tpms)H(CO)$_3$] (**5**), which was isolated in good yield as a green powder. The compound is significantly air-sensitive as a solid and highly sensitive in solution; it turned immediately to black in the presence of O$_2$. It is sparingly soluble in water ($S_{25\,°\mathrm{C}} \approx$ 1 mg mL^{-1}). The three carbonyl stretching absorptions in the solid-state IR spectrum (2025, 1945 and 1912 cm^{-1}) are indicative of a C_s seven-coordinate structure, as observed for the previously described complex **3** and other related hydride complexes that involve a facially coordinating ligand.[41,52–54] The lower *ν*(CO) values of **5** as compared to those of **3** reflect the stronger electronegativity of iodide relative to hydride and therefore the higher metal-electron density in the latter, as observed for similar systems.[38,41,52,55] In contrast, **5** displays higher *ν*(CO) values than the Tp analogue [Mo(Tp)H(CO)$_3$] (2000, 1906, 1887 cm^{-1}, in THF),[41] which is consistent with the weaker electron-donor ability of Tpms in comparison with Tp (see above). The ^{1}H NMR spectrum (CDCl$_3$) exhibits one set of equivalent pyrazolyl rings, thereby suggesting a fluxional behaviour. The chemical shift for the hydridic proton (*δ* = –3.23 ppm) is similar to those reported for [Mo(Tpm)H(CO)$_3$][BF$_4$] (*δ* = –3.12 ppm)[38] and analogous Tp compounds.[41,52–54]

By slow evaporation of a solution of **5** in chloroform, reddish-brown crystals were obtained. The X-ray diffraction analysis disclosed the structure of the oxidized [{Mo(Tpms)OCl}$_2$](μ-O) complex **6** (Scheme 1), which

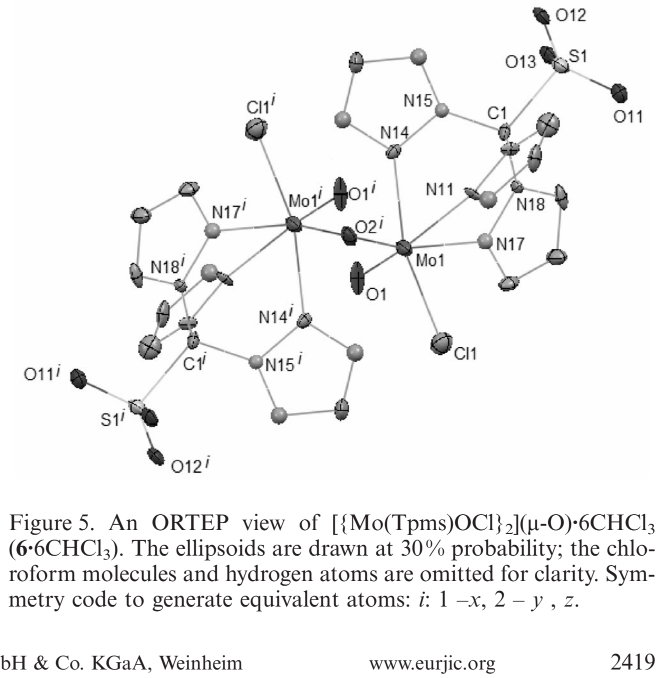


Figure 5. An ORTEP view of [{Mo(Tpms)OCl}$_2$](μ-O)·6CHCl$_3$ (**6**·6CHCl$_3$). The ellipsoids are drawn at 30% probability; the chloroform molecules and hydrogen atoms are omitted for clarity. Symmetry code to generate equivalent atoms: *i*: 1 –*x*, 2 – *y* , *z*.

crystallized with six chloroform molecules. An ORTEP drawing of complex **6** is shown in Figure 5. Due to the rather poor quality of this structure, only a restricted discussion is presented. The asymmetric unit contains half of the molecule, with the bridging O2 atom sitting on an inversion centre, which imposes a perfect linearity to the Mo–O–Mo group. The molecule includes two terminal oxygen atoms, displaying the well-known $(Mo_2O_3)^{4+}$ moiety. Each Mo^V centre adopts a pseudo-octahedral coordination geometry with the anionic tridentate Tpms ligand bonding facially the metal atom. A similar structure containing the related hydrotris(1-pyrazolyl)borate ligand has been described previously.[56]

Reactions of Li[Mo(Tpms)(CO)$_3$] (1) with AgBF$_4$

Reaction of compound **1** with $AgBF_4$ (1 equiv.) in thf gave a reddish-brown powder which, upon attempted crystallization by slow diffusion of Et_2O into a thf solution, afforded yellow crystals of product **7** suitable for X-ray diffraction analysis. Compound **7** is the oxo–Mo^{VI} complex $[\{Mo(Tpms)O_2\}_2](\mu\text{-}O)$, which crystallized with one molecule of thf. The two anionic tris(1-pyrazolyl)methanesulfonate groups in the molecule (Figure 6) act as κ^3:*N,N,N* ligands and facially bond the Mo^{VI} centres, which display the well-known $(Mo_2O_5)^{2+}$ bridging structure found in many related cyclopentadienyl-containing compounds.[57–60] Each molybdenum atom bears two terminal oxo ligands and displays a pseudo-octahedral geometry, with the two heavily distorted octahedra sharing the O2 atom as common vertices. Such a distortion may be a consequence of the large intramolecular repulsion between each pair of oxo ligands [O1–Mo1–O3 and O4–Mo2–O6 angles of 104.47(16)° and 104.87(15)°, respectively]. The deviation of the Mo1–O2–Mo1 angle [176.14(16)°] from linearity can be ascribed to packing forces in the crystal, as it has already been recognized in other cases.[57,58] The Mo=O and Mo–O–Mo bond lengths [in the 1.689(3)–1.694(3) and 1.879(3)–1.884(3) Å ranges, respectively] agree with their double- and single-bond character, respectively. The structure is stabilized by intramolecular π–π stacking contacts. The N17–N18 and the N21–N22 pyrazole rings are mutually involved in a face-to-face interaction with a distance of 3.627 Å between the ring centroids, the H17 hydrogen atom of the former ring being directed towards the N24–N25 pyrazolyl π cloud and the H21 atom of the latter being directed towards the N14–N15 pyrazolyl π cloud (H17···centroid 2.771 Å, C17–H17···centroid 150.13°; H21···centroid 2.747 Å, C21–H21···centroid 149.95°).

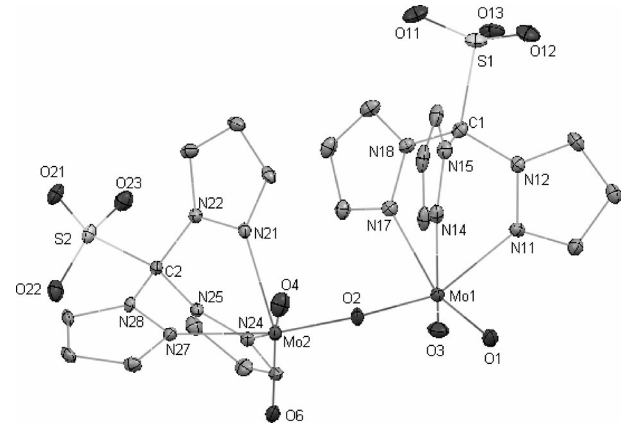


Figure 6. An ORTEP view of $[\{Mo(Tpms)O_2\}_2](\mu\text{-}O)\cdot thf$ (**7**·thf). The ellipsoids are drawn at 30% probability; the thf molecule and hydrogen atoms are omitted for clarity. Selected distances [Å]: Mo1–N11 2.214(3), Mo1–N14 2.302(3), Mo1–N17 2.308(3), Mo1–O1 1.690(3), Mo1–O2 1.879(3), Mo1–O3 1.689(3), Mo2–N21 2.312(3), Mo2–N24 2.255(3), Mo2–N27 2.194(3), Mo2–O2 1.884(3), Mo2–O4 1.692(3), Mo2–O6 1.694(3), S1–O11 1.438(3), S1–O12 1.435(3), S1–O13 1.436(3). Selected angles [°]: N11–Mo1–N14 74.20(12), N11–Mo1–N17 74.66(11), N14–Mo1–N17 74.78(11), O1–Mo1–O3 104.47(16), N21–Mo2–N24 74.31(11), N21–Mo2–N27 74.70(11), N24–Mo2–N77 75.82(12), O4–Mo1–O6 104.87(15), Mo1–O2–Mo2 176.14(16).

Electrochemical Behaviour

Complexes Li[Mo(Tpms)(CO)$_3$] (**1**), [Mo(Tpms)I(CO)$_3$] (**3**) and [Mo(Tpms)H(CO)$_3$] (**5**) exhibit, by cyclic voltammetry (at 200 mV s^{-1}) at a platinum electrode and in 0.2 M [nBu$_4$N][BF$_4$]/CH$_2$Cl$_2$ (Figure 7), a single-electron reversible (for **1**) or irreversible (for **3** and **5**) oxidation wave (wave **I**) at ${}^{\mathbf{I}}E_{1/2}^{ox} = -0.35$ (**1**), ${}^{\mathbf{I}}E_{p}^{ox} = -0.09$ (**3**) and –0.44 (**5**) V versus the ferrocene/ferrocinium redox pair (Fc/Fc$^+$), which are assigned to the $Mo^0 \rightarrow Mo^I$ (**1**) or to the $Mo^{II} \rightarrow Mo^{III}$ (**3** and **5**) oxidation processes. It is followed, at a higher potential, by a second reversible (for **3**) or irreversible (for **1** and **5**) anodic wave (wave **II**) at 0.60 (**1**), 0.18 (**3**) or 0.51 (**5**) V versus Fc/Fc$^+$, respectively.

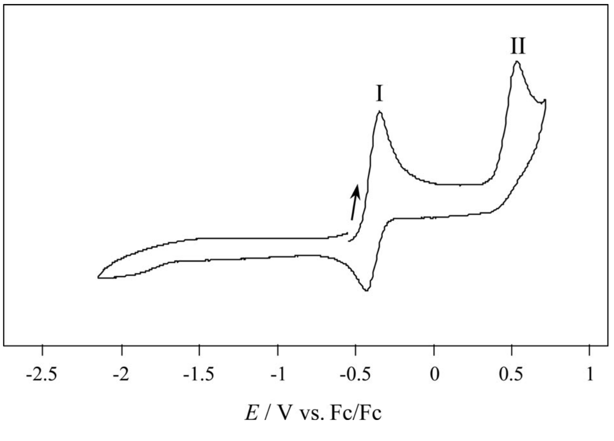


Figure 7. Cyclic voltammogram of Li[Mo(Tpms)(CO)$_3$] (**1**) (1.6 mM) (initial anodic scan), at a Pt electrode, in 0.2 M [nBu$_4$N][BF$_4$]/CH$_2$Cl$_2$ (v = 200 mV/s).

In complex **1**, the second oxidation process is assigned to the further oxidation that yields the 16-electron [Mo(Tpms)(CO)$_3$]$^+$ complex of Mo^{II}, its irreversibility being probably associated to fast coordination of a solvent molecule, thereby yielding an electronically saturated product. The irreversibility of the first oxidation wave of compounds **3** and **5** signals the instability of the resulting cationic Mo^{III} complexes, which then rapidly decompose with probable CO loss[61] and, for the hydride compound **5**, by deprotonation.[62–65]

The first oxidation potentials of all these tricarbonyl complexes are much lower than that of the parent hexacarbonyl compound (0.98 V vs Fc/Fc^+) on account of the replacement of three carbonyl groups in the latter by other more electron-donating ligands.[66–69] The lower first oxidation potential of **5** in comparison with **3** reflects the stronger electron-donor character of the hydride relatively to the iodide ligand.[68]

The first oxidation potential of the Mo^0 complex **1** (–0.35 V vs Fc/Fc^+) is comparable to those (in the –0.53 to –0.23 V vs Fc/Fc^+ range) reported for analogous molybdenum complexes of the type $[\mathbf{L}Mo(CO)_3]^n$, in which **L** is a tridentate N-donor ligand [Tp (n = –1),[70] Tpm^{Me} (n = 0),[71] 1,4,7-trimethyl-1,4,7-triazacyclononane (n = 0),[72] or 1,4,7-tribenzyl-1,4,7-triazacyclononane (n = 0)],[70] thus reflecting[66–68,73–75] the relative donor/acceptor abilities of these different **L** ligands. The more negative value (–0.53 V vs Fc/Fc^+) is reported[70] for complex $[Mo(Tp)(CO)_3]^-$ and the less negative one (–0.234 V vs. Fc/Fc^+) for $[Mo(Tpm^{Me})(CO)_3]$,[71] whereas that of **1** is intermediate, in accord with the order of the net electron-donor ability of the corresponding tripodal ligands. This is shown by the values of the electrochemical Lever parameter (E_L; the lower this value, the stronger the ligand electron-donor character) that parallel the above $E_{1/2}^{ox}$ values of the complexes: E_L = –0.23 V (Tp),[76] –0.09 V (Tpms)[27] and 0.14 V (Tpm).[77]

In addition, the hydride complex $[Mo(Tpms)H(CO)_3]$ (**5**) is oxidized at a higher potential (–0.44 V) relative to the following related hydride compounds, in the order: $[Mo(Cp)H(CO)_3]$ (–0.50 V)[78] > $[Mo(Tp)H(CO)_3]$ (–0.53 V)[78] > $[Mo(Tp^*)H(CO)_3]$ (–0.59 V)[78] [Tp* = hydrotris(3,5-dimethylpyrazolyl)borate] > $[Mo(Cp^*)H(CO)_3]$ (–0.71 V)[78] (values are vs the ferrocene/ferrocenium redox couple). This points out the following order of the electron-donor ability of the involved polyhapto ligands, also in agreement with the IR results discussed above and with the electron donation by the methyl substituents: Tpms < Cp < Tp < Tp* < Cp*.

Conclusion

This work shows that $[Mo(CO)_6]$ is a convenient starting material for the syntheses of both low- and high-oxidation-state molybdenum complexes that bear the sulfonated Tpms ligand. In fact, three carbonyl groups are readily displaced by the Tpms tripodal ligand to afford a tricarbonyl Tpms–Mo^0 complex **1**, which, upon metal halogenation or protonation, forms seven-coordinate Tpms–Mo^{II} complexes **3** and **5**. The latter are oxidized with air to form high-oxidation-state dinuclear Tpms–oxo–Mo complexes that bear the $\{Mo^V_2O_2(\mu\text{-}O)_2\}^{2+}$ and $\{Mo^V_2O_2Cl_2(\mu\text{-}O)\}^{2+}$ moieties, the latter upon chlorination with $CHCl_3$. The Tpms–oxo–Mo^{VI} complex, on the other hand, contains the $\{Mo^{VI}_2O_4(\mu\text{-}O)\}^{2+}$ unit and was obtained by oxidation of the above Tpms–Mo^0 compound **1**. Hence, the low-oxidation-state Tpms–Mo^0 complex provides a versatile entry to a diversity of high-oxidation-state Tpms–oxo–Mo species.

Interestingly, the sulfonate group of the Tpms ligand is not innocent and plays a determining role on the properties of some of the complexes, not only by imparting hydrosolubility, but also by coordinating to the molybdenum atom (in **4**) or to the Li^+ ion of a contiguous molecule that forms a 1D polymeric chain (in **2** and also in the $[Li(Tpms)]_n$ salt).

The above features of the sulfonate group of Tpms deserve to be further explored for the syntheses of other water-soluble (i) organometallic low-oxidation-state Mo complexes, (ii) middle- and high-oxidation-state Mo compounds, and (iii) polymeric and supramolecular assemblies.

In addition, the availability of comparable Tp, Tp*, Cp and Cp* complexes allows the ordering of the corresponding and related polyhapto ligands according to their electron-donor character on the basis of the oxidation potentials of those complexes, as measured by cyclic voltammetry, which provides a rather convenient tool for this purpose.

Experimental Section

General Techniques: Unless stated otherwise, all preparations and manipulations were carried out with Schlenk techniques under an oxygen-free argon atmosphere. All glassware was oven-dried at 120 °C. Tetrahydrofuran and diethyl ether were dried with Na/benzophenone, toluene was dried with Na, and pentane and dichloromethane were dried with CaH_2. Each of them was distilled under dinitrogen prior to use.

Materials and Instrumentation: IR spectra were recorded with a BIO-RAD FTS 3000MX spectrophotometer, in KBr pellets. Wavenumbers are in cm^{-1}; abbreviations: vs = very strong, s = strong, m = medium, w = weak, br. = broad. ^1H NMR spectra were recorded with a Bruker Avance II 300 operating at 300 MHz. Chemical shifts were measured relative to residual solvent proton resonances and are expressed in ppm downfield from Me_4Si. Coupling constants are given in Hertz. Abbreviations: s = singlet, d = doublet, m = complex multiplet, dd = doublet of doublets, br = broad.

The electrochemical experiments were performed with an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a general purpose interface bus (GPIB). Cyclic voltammograms were obtained in 0.2 M $[nBu_4N][BF_4]$ in CH_2Cl_2, at a platinum disc working electrode (d = 1 mm) and at 25 °C. A Luggin capillary connected to a silver wire pseudoreference electrode was used to control the working electrode potential, and a Pt wire was employed as the counter electrode. The redox potentials of the complexes were measured by cyclic voltammetry and their values are quoted relative to the saturated calomel electrode (SCE) by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.525 V vs SCE in CH_2Cl_2[79]) as internal standard. Hydrotris(1-pyrazolyl)methane and lithium tris(1-pyrazolyl)methanesulfonate were prepared in accordance with published procedures.[25,80] Mass spectra were recorded with a Varian 500-MS LC Ion Trap mass spectrometer equipped with an ESI interface. Mass spectra were obtained by scanning the mass analyzer from m/z = 50 to 2000 with a total of three microscans. Elemental analyses were carried out at the Analytical Laboratory of the Instituto Superior Técnico, Universidade Técnica de Lisboa.

Preparation of Complexes

Lithium Tricarbonyl[tris(1-pyrazolyl)methanesulfonato]molybdenum(0) {Li[Mo(Tpms)(CO)$_3$] (1)} and its Conversion to [Mo(Tpms)(CO)$_2$(μ-CO)Li(thf)$_2$]$_n$ (2): A suspension of [Mo(CO)$_6$] (0.1420 g, 0.538 mmol) and Li(Tpms) (0.1774 g, 0.591 mmol) was heated at reflux in CH_3CN (60 mL) for 6 h under a dinitrogen atmosphere. The initially white suspension turned into a clear yellow solution and then to green. After cooling to 20 °C, the reaction mixture was filtered to remove the unreacted ligand (not very soluble in CH_3CN), and the resulting solution was evaporated under reduced pressure to afford a yellowish-green powder of **1** in quantitative yield. Compound **1** is readily soluble in water ($S_{25\,^{\circ}C} \approx 16\,mg\,mL^{-1}$) and in other polar solvents such as MeOH, CH_3CN, thf, $CHCl_3$ and CH_2Cl_2. ^{1}H NMR (300 MHz, CD_3OD, 20 °C): δ = 8.84 [d, $^3J_{H,H}$ = 3.0 Hz, 3 H, H(5) or H(3), pyrazolyl], 7.97 [d, $^3J_{H,H}$ = 1.9 Hz, 3 H, H(3) or H(5), pyrazolyl], 6.36 [dd, $^3J_{H,H}$ = 2.9 Hz, 3 H, H(4) pyrazolyl] ppm. ^{13}C NMR (75.5 MHz, CD_3OD, 20 °C): δ = 146.12 [s, C(3) or C(5), pyrazolyl], 135.86 [s, C(5) or C(3) pyrazolyl], 106.59 [s, C(4), pyrazolyl] ppm. IR (KBr pellet): $\tilde{\nu}$(CO) = 1916, 1756 cm^{-1}. MS (ESI, CH_3CN): m/z = 475.3 [M$^-$].

For recrystallization, the above yellowish-green solid of **1** was dissolved in thf, then Et_2O was slowly diffused into it to afford suitable crystals of **2**. $C_{13}H_9LiMoN_6O_6S\cdot2thf$ (624.4): calcd. C 40.4, N 13.5, H 4.0; found C 40.6, N 13.1, H 4.0.

Lithium Tris(1-pyrazolyl)methanesulfonate Ligand [LiTpms]$_n$: CH_3CN (5 mL) was added to the unreacted ligand, isolated by filtration (see above) in the synthesis of **1**, and to increase the solubility of the compound, the mixture was heated to around 85 °C for 30 min. The hot solution was then filtered into an open flask and slowly cooled to room temperature, thereby affording white crystals of polymeric [LiTpms]$_n$ suitable for X-ray analysis.

Tricarbonyliodo[tris(1-pyrazolyl)methanesulfonato]molybdenum(II) {[Mo(Tpms)I(CO)$_3$] (3)}: One equivalent of elemental I_2 (0.0693 g, 0.273 mmol) was added to a solution of **1** (0.131 g, 0.273 mmol) in CH_3CN (20 mL), thereby resulting in a colour change of the reaction mixture from green to reddish-brown. After 1 h, the solution was taken to dryness under vacuum and the resulting reddish-brown solid was extracted with 15 mL of a 1:1 $CHCl_3$/thf mixture. After filtration, the solution was evaporated under reduced pressure to afford a reddish-brown powder of **3**. Yield: 0.098 g (0.164 mmol, 60%). Compound **3** is readily soluble in chlorinated hydrocarbons, CH_3CN, thf and also in water ($S_{25\,^{\circ}C} \approx 5\,mg\,mL^{-1}$), but not considerably soluble in alcohols, diethyl ether and hydrocarbon solvents. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 9.17 [d, $^3J_{H,H}$ = 2.9 Hz, 3 H, H(5) or H(3), pyrazolyl], 8.51 [d, $^3J_{H,H}$ = 2.2 Hz, 3 H, H(3) or H(5), pyrazolyl], 6.56 [dd, $^3J_{H,H}$ = 2.7 Hz, 3 H, H(4) pyrazolyl] ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 148.94 [s, C(5) or C(3) pyrazolyl], 138.08 [s, C(3) or C(5), pyrazolyl], 107.96 [s, *C*(4), pyrazolyl] ppm. IR (KBr pellet): $\tilde{\nu}$(CO) = 2039, 1966, 1944 cm^{-1}. $C_{13}H_9IMoN_6O_6S\cdot1.5thf\cdot CHCl_3\cdot2H_2O$ (864.0): calcd. C 27.8, N 9.7, H 3.0; found C 27.0, N 9.4, H 3.2.

Tetraoxobis[tris(1-pyrazolyl)methanesulfonato]dimolybdenum(V) {[{Mo(Tpms)O(μ-O)}$_2$] (4)}: Reddish-brown crystals of **4**·2CH_3CN suitable for X-ray analysis were obtained upon slow diffusion of Et_2O into a solution of complex **3** in CH_3CN. ^{1}H NMR [300 MHz, $(CD_3)_2CO$, 20 °C]: δ = 9.19 [m, 6 H, H(5) or H(3), pyrazolyl], 7.53 [m, 6 H, H(3) or H(5), pyrazolyl], 6.63 [m, 6 H, H(4) pyrazolyl] ppm. ^{13}C NMR [75.5 MHz, $(CD_3)_2CO$, 20 °C]: δ = 167.59 [s, 3 C, C(5) or C(3) pyrazolyl], 145.23 [s, 3 C, C(3) or C(5), pyrazolyl], 95.10 [s, 3 C, C(4), pyrazolyl] ppm. IR (KBr): $\tilde{\nu}$ = 1104, 1073, 1056, 1032 (br. s, S=O, Mo=O), 803 (s, Mo–O–Mo) cm^{-1}.

Tricarbonylhydrido[tris(1-pyrazolyl)methanesulfonato]molybdenum(II) {[Mo(Tpms)H(CO)$_3$] (5)}: Complex **1** (130 mg, 0.2715 mmol) was dissolved in CH_3CN (30 mL) at 20 °C. HBF_4 (69.42 μL, 54% in diethyl ether, 0.5068 mmol) was added dropwise, thereby resulting in a colour change of the reaction mixture from greenish-yellow to green. After 1 h, the reaction mixture was taken to dryness under vacuum and the resulting solid was extracted with distilled CH_3COCH_3 (5 mL). The suspension was filtered and the resulting solution was evaporated under reduced pressure to afford **5** as a green powder. Yield: 0.085 g (0.18 mmol, 66%). Compound **5** is soluble in acetonitrile and chloroform and sparingly soluble in water ($S_{25\,^{\circ}C} \approx 1\,mg\,mL^{-1}$). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 9.05 [d, $^3J_{H,H}$ = 2.9 Hz, 3 H, H(5) or H(3), pyrazolyl], 8.08 [d, $^3J_{H,H}$ = 2.2 Hz, 3 H, H(3) or H(5), pyrazolyl], 6.46 [dd, $^3J_{H,H}$ = 2.7 Hz, 3 H, H(4) pyrazolyl], –3.23 (s, 1 H, MoH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 147.42 [s, C(5) or C(3) pyrazolyl], 137.24 [s, C(3) or C(5), pyrazolyl], 107.36 [s, C(4), pyrazolyl] ppm. IR (KBr pellet): $\tilde{\nu}$(CO) = 2025, 1945, 1912 cm^{-1}. MS (ESI, CH_3CN): m/z = 475.3 [M$^-$]. $C_{13}H_{10}MoN_6O_6S\cdot2CH_3COCH_3$ (590.4): calcd. C 38.7, N 14.2, H 3.7; found C 38.8, N 14.0, H 3.5.

Dichlorotrioxobis[tris(1-pyrazolyl)methanesulfonato]dimolybdenum(V) {[{Mo(Tpms)OCl}$_2$](μ-O) (6)}: Reddish-brown crystals of **6**·6$CHCl_3$ suitable for X-ray analysis were obtained, in the presence of air, by slow evaporation of a solution of **5** in chloroform. IR (KBr): $\tilde{\nu}$ = 1095, 1079, 1057, 1030 (br. s, S=O, Mo=O), 802 (s, Mo–O–Mo) cm^{-1}.

Pentaoxobis[tris(1-pyrazolyl)methanesulfonato]dimolybdenum(VI) {[{Mo(Tpms)O$_2$}$_2$](μ-O) (7)}: $AgBF_4$ (40.5 mg, 0.208 mmol) was dissolved in thf (10 mL) and added to a solution of **1** (100 mg, 0.208 mmol) in thf (10 mL) at 20 °C. The colour of the reaction mixture immediately changed from green to red and a black solid (Ag) started to precipitate. The suspension was filtered and the resulting reddish solution was evaporated under reduced pressure to afford a reddish brown powder. This crude solid was washed twice with CH_3CN (10 mL) and dried under vacuum. Slow diffusion of Et_2O into a solution of this crude solid in thf afforded, in the presence of air, yellow crystals of **7**·thf that were suitable for X-ray analysis. IR (KBr): $\tilde{\nu}$ = 1080, 1070, 1040 (br. s, S=O, Mo=O), 916 (w, M=O), 801 (s, Mo–O–Mo) cm^{-1}.

Crystal Structure Determinations: Single crystals of [LiTpms]$_n$, **2**, **4**, **6** and **7** were obtained as indicated above. Intensity data were collected at 150 K with a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. Data were collected using omega scans of 0.5° per frame and full spheres of data were obtained. Cell parameters were retrieved with Bruker SMART software and refined with Bruker SAINT[81] on all the observed reflections. Absorption corrections were applied using SADABS.[81] Structures were solved by direct methods by using the SHELXS–97 package[82] and refined with SHELXL–97.[83] Calculations were performed using the WinGX System, Version 1.80.03.[84] All hydrogen atoms were inserted in calculated positions. Least-squares refinements with anisotropic thermal motion parameters for all the non-hydrogen (except C17, N22 and N27 of [LiTpms]$_n$, which were refined isotropically) atoms and isotropic for the remaining atoms were employed. Crystal data and refinement parameters are shown in Table 1.

CCDC-749680 {for [Li(Tpms)]$_n$}, -749681 (for **2**), -749682 (for **4**·2CH_3CN), -749683 (for **6**·6$CHCl_3$) and -749684 (for **7**·thf) contain the supplementary crystallographic data for this paper. These

Table 1. Selected crystallographic and refinement parameters for compounds $[LiTpms]_n$, **2**, **4**·$2CH_3CN$, **6**·$6CHCl_3$ and **7**·thf.

	$[LiTpms]_n$	**2**	**4**·$2CH_3CN$	**6**·$6CHCl_3$	**7**·thf
Empirical formula	$C_{20}H_{18}Li_2N_{12}O_6S_2$	$C_{21}H_{25}LiMoN_6O_8S$	$C_{24}H_{24}Mo_2N_{14}O_{10}S_2$	$C_{26}H_{24}Cl_{20}Mo_2N_{12}O_9S_2$	$C_{24}H_{26}Mo_2N_{12}O_{12}S_2$
Formula weight	600.46	624.42	924.57	1613.57	930.57
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
Space group	*Pca*21	$P\bar{1}$	*C*2/*c*	$P2_1/c$	$P2_1/n$
a [Å]	18.6055(15)	10.469(2)	18.3013(5)	12.157(2)	13.222(3)
b [Å]	8.3363(9)	10.794(2)	13.4344(4)	12.716(3)	19.685(4)
c [Å]	16.6854(14)	11.685(4)	15.2516(4)	18.007(4)	14.048(3)
α [°]	90	90.156(17)	90	90	90
β [°]	90	99.50(2)	116.8860(10)	99.255(13)	117.084(5)
γ [°]	90	94.365(18)	90	90	90
Volume [Å^3]	2587.9(4)	1298.4(6)	3344.53(16)	2747.6(10)	3255.4(12)
Z	4	2	4	2	4
Density (calcd.) [$Mg m^{-3}$]	1.541	1.597	1.836	1.950	1.899
Absorption coefficient [mm^{-1}]	0.269	0.642	0.951	1.563	0.981
F(000)	1232	636	1848	1584	1864
Reflections collected	11746	17721	8097	16985	14365
Unique reflections	4493	4576	3045	5004	4725
R_{int}	0.1589	0.1106	0.0329	0.2844	0.0418
GOF	0.935	0.964	1.061	0.954	1.037
Final R_1, wR_2 ($I \geq 2\sigma$)[a]	0.0775, 0.1636	0.0538, 0.1016	0.0280, 0.0681	0.0949, 0.1676	0.0357, 0.0864
R_1, wR_2 (all data)	0.1577, 0.2151	0.1016, 0.1189	0.0364, 0.0717	0.2572, 0.2349	0.0465, 0.0920

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$.

data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ESI-MS of an NCMe solution of $Li[TpmsMo(CO)_3$ (Figure S1), fragment of the infinite 1D polymer chain in the crystal cell of $[Li(SO_3)C(pz)_3]_n$ (Figure S2) and crystal packing diagrams of compound **2** (Figures S3 and S4).

Acknowledgments

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