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<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p> <p>Figure 1.cdx Figure 6.cdx</p>	



## ARTICLE

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# Structural Characterization and Theoretical Calculations of *cis*-Dioxo(N-salicylidene-2-aminophenolato)(ethanol)molybdenum(VI) complexes MoO<sub>2</sub>(SAP)(EtOH) (SAP = N-salicylidene-2 aminophenolato)

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*Dedicated to Professor Dr. Michael Veith on the Occasion of his 65<sup>th</sup> Birthday.*

**Keywords:** Molybdenum; X-ray crystallography; Theoretical calculations; Schiff bases; Tridentate ligands

The crystal structure of MoO<sub>2</sub>(SAP)(EtOH) is reported herein for the first time. The compound crystallizes in the monoclinic crystallographic system (*P*2<sub>1</sub>/*n*, *a* = 11.0923(3) Å, *b* = 6.9590(2) Å, *c* = 19.4499(5) Å, β = 94.458(1)°, *V* = 1496.82(7) Å<sup>3</sup>, *Z* = 4). The molybdenum atom adopts a distorted octahedral geometry with *cis* Mo=O bonds, typical of *cis*-dioxomolybdenum(VI) complexes. The ethanol ligand is situated *trans* to one oxido ligand. Theoretical calculations in the gas phase have been performed to examine the relative stability of MoO<sub>2</sub>(L)(EtOH) and the [MoO<sub>2</sub>(L)]<sub>2</sub> dimeric form (L= SAP, SAE).

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 Supporting information for this article is available from the author.

The formation of either of these species strongly depends on the nature of the ligand L that surrounds the metal centre, the choice of solvent, the presence of other donor molecules D, and the product isolation conditions.

For example, Rajan and Chakravorty [7] reported the thermal conversion of the complex MoO<sub>2</sub>L(D) (L = SAE, SAP, and their peripheral-substituted analogues) to [MoO<sub>2</sub>L]<sub>2</sub> (see Fig. 1) The authors described that in order to isolate the complex MoO<sub>2</sub>(SAP)(EtOH) they had to reflux MoO<sub>2</sub>(acac)<sub>2</sub> and SAPH<sub>2</sub> in ethanol. By this method, no formation of dimeric species was observed [7,10]. However, a dimeric species with stoichiometry [MoO<sub>2</sub>(SAP)]<sub>2</sub> was obtained by heating solid MoO<sub>2</sub>(SAP)(EtOH) at 100°C under vacuum [7,11]. The formation of the oxygen bridge in the resulting [Mo(O)(μ-O)(SAP)]<sub>2</sub> molecule was evidenced by IR spectroscopy with the appearance of an intense band between 800 and 850 cm<sup>-1</sup> [12].

A recent report by Cindrić [13] suggests that a monomeric structural analogue of the molybdenum(VI)-SAP species, the complex MoO<sub>2</sub>(SAE)(EtOH), can be synthesized by a different procedure. Here, reaction of MoO<sub>2</sub>(acac)<sub>2</sub> with aldehyde and amino-ethanol followed by warming up in a mixture of CH<sub>2</sub>Cl<sub>2</sub>/EtOH (1:1) resulted in formation of the desired product [13]. The described thermal gravimetric analysis (TGA) of MoO<sub>2</sub>(SAE)(EtOH) indicated that the coordinating ethanol molecule is very labile (loss between 66°C and 83°C vs. 100°C for the corresponding MoO<sub>2</sub>(SAP)(EtOH) monomer).

## Introduction

Metal oxides are among the most efficient complexes in catalysis. In terms of molecular catalysts, several complexes have been employed for their peculiar reactivity towards oxo-transfer [1-3]. We are currently interested in molybdenum chemistry [4] since its major role in biological processes has been demonstrated over the last two decades [5]. Molecular dioxomolybdenum(VI) complexes are promising candidates as epoxidation catalysts and furthermore can be easily obtained by standard synthetic procedures [6]. Complexes of type MoO<sub>2</sub>L, L being a tridentate dianionic Schiff base ligand [N-salicylidene-2-aminophenolato (SAP<sup>2-</sup>) or N-salicylidene-2-aminoethanolato (SAE<sup>2-</sup>)] have received great attention and the synthetic access towards these molecules has been reported by several research groups [7-9]. In this theme, the known members of this family can be mononuclear, MoO<sub>2</sub>L(D), stabilized by a donor molecule D such as an appropriate solvent, or dinuclear containing a double oxygen bridge (i.e. [MoO<sub>2</sub>L]<sub>2</sub>).

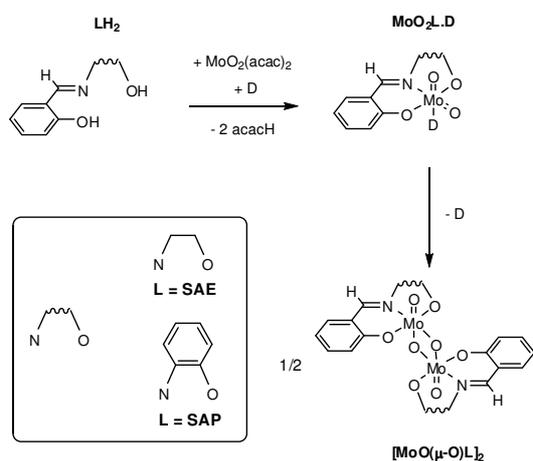


Figure 1. Synthetic routes towards  $\text{MoO}_2\text{L.D}$  and  $[\text{Mo}(\text{O})(\mu\text{-O})\text{L}]_2$  complexes (L = SAE and SAP)

However, following the earlier mentioned experimental procedure by Rajan and Chakravorty in neat ethanol and utilizing the ligand SAE, Sobczak and co-workers reported the direct isolation of dimeric  $[\text{Mo}(\text{O})(\mu\text{-O})(\text{SAE})]_2$  in solution [12]. The complex was characterized by X-ray-crystallography and additionally, IR and Raman spectroscopy data were presented. It is worth mentioning that this dimer can be easily converted back into a mononuclear species,  $\text{MoO}_2(\text{SAE})(\text{MeOH})$ , in refluxing methanol [8].

These observations motivated us to perform calculations on the relative stability in the gas phase between  $\text{MoO}_2\text{L}(\text{EtOH})$  and  $[\text{MoO}_2\text{L}]_2$  complexes (L = SAP and SAE) in order to better understand under which conditions monomeric or dimeric species are preferentially formed.

Although  $\text{MoO}_2(\text{SAP})(\text{EtOH})$  has been already reported in the literature, [7,10,12,14-16] and several X-ray structures of substituted- $\text{MoO}_2(\text{SAP})(\text{D})$  have been described [17], the X-ray structure of the title compound  $\text{MoO}_2(\text{SAP})(\text{EtOH})$  is presented herein for the first time.

## Results and Discussion

### X-ray Diffraction analysis of $\text{MoO}_2(\text{SAP})(\text{EtOH})$

The compound crystallizes in the monoclinic  $P2_1/n$  space group (see Table 1). The crystal structure shows the  $\text{MoO}_2(\text{SAP})$  fragment stabilized by the coordination of one EtOH molecule (see Figure 2). The Mo(1) atom is coordinated in octahedral geometry by two *cis* oxido atoms O(3) and O(4), by the SAP ligand with the N(1), O(1) and O(2) atoms occupying meridional positions and finally by the O(5) atom from the coordinated ethanol molecule. The most significant geometric parameters are collected in Table 2. The Mo-oxido bonds lengths and the O(3)-Mo(1)-O(4) angle between the two Mo-oxido bonds are in agreement with those found for similar  $\text{MoO}_2$  compounds [17]. The SAP ligand is not planar, the dihedral angle between the two

aromatic rings being  $9.52^\circ$ . The O(1)-Mo(1) and O(2)-Mo(1) bonds corresponding to the O-linkage of molybdenum atom to SAP ligand are respectively  $1.972(3)$  Å and  $1.914(3)$  Å. The shorter Mo-O bond length is related to the six-membered ring. The imine N is rather loosely bonded to the Mo atom [ $2.291(4)$  Å] because of the strong *trans* influence of the O(4) atom.

In the unit cell, centrosymmetric pseudo-dimers are formed by the establishment of hydrogen bonds between the H-O hydrogen of the ethanol molecule of one complex and one oxygen atom O(1) from the five atom ring of a second complex, as shown in Figure 3. This arrangement is rather typical of small-sized substituted SAP complexes [17]. The O(5)⋯O(1)' distance of  $2.482(3)$  Å is in accordance with the existence of hydrogen bonding [13,17].

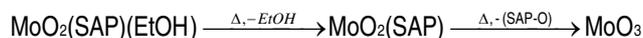
Table 1. Crystal Structure Data and structure refinement for  $\text{MoO}_2(\text{SAP})(\text{EtOH})$

Compound	$\text{MoO}_2(\text{SAP})(\text{EtOH})$
Empirical formula	$\text{C}_{15}\text{H}_{15}\text{Mo}_1\text{N}_1\text{O}_5$
Formula weight	385.22 g/mol
$\lambda$	$0.71073$ Å (MoK $\alpha$ )
T	296(2) K
Crystal System	Monoclinic
Space group	$P2_1/n$
A	$11.0923(3)$ Å
B	$6.9590(2)$ Å
C	$19.4499(5)$ Å
$\beta$	$94.4580(10)^\circ$
V	$1496.82(7)$ Å <sup>3</sup>
Z	4
$D_{\text{calc}}$	$1.709$ Mg.m <sup>-3</sup>
Absorption coefficient	$0.899$ mm <sup>-1</sup>
F(000)	776
$\theta$ range (min-max)	$3.11^\circ$ - $28.31^\circ$
Crystal size	$0.10 \times 0.15 \times 0.33$ mm <sup>3</sup>
Index ranges (h, k, l)	$-14 \leq h \leq 14$ $-9 \leq k \leq 9$ $-25 \leq l \leq 25$
Reflections collected	31249
Independent reflections	3710 [R(int) = 0.0381]
Data / restraints / parameters	3710 / 0 / 200
Final $R_1/wR_2$ [ $I > 2\sigma(I)$ ]	0.0401 / 0.0862
Absorption correction	Semi-empirical from equivalents ( $T_{\text{min}} = 0.654/T_{\text{max}} = 1.0$ )
Goodness-of-fit on $F^2$	1.018
Largest diff. peak/hole	$1.825$ and $-0.562$ e.Å <sup>-3</sup>

### TGA measurements.

Analyses of the loss of ethanol for  $\text{MoO}_2(\text{SAP})(\text{EtOH})$  have been reported previously [7,10]. The thermogravimetric analysis of  $\text{MoO}_2(\text{SAP})(\text{EtOH})$  has been performed herein using air as gas carrier. The sample was heated at a rate of  $0.83^\circ\text{C s}^{-1}$  from  $20^\circ\text{C}$  to  $600^\circ\text{C}$ . A first endothermic weight loss is observed between  $100^\circ\text{C}$  and  $120^\circ\text{C}$ , previously assigned [7,10] to the loss of one molecule of ethanol. The experimental mass loss value ( $\Delta m_{\text{rel}} = 11.80\%$ ) agrees with the expected one ( $\Delta m_{\text{rel}} = 11.96\%$ ).

Our TGA study has been pushed to much higher temperatures than previously reported, see Figure 4. An exothermic loss observed in the temperature range 280°C–550°C corresponds to the loss of an organic fragment corresponding to (C<sub>13</sub>H<sub>9</sub>NO), with an experimental value ( $\Delta m_{\text{rel}} = 51.64\%$ ) in accordance with the expected mass loss ( $\Delta m_{\text{rel}} = 50.68\%$ ). Thus, the final product of this thermal decomposition process corresponds to MoO<sub>3</sub>, which is stable under these conditions [18] (see scheme 1).



Scheme 1. Thermal decomposition of MoO<sub>2</sub>(SAP)(EtOH).

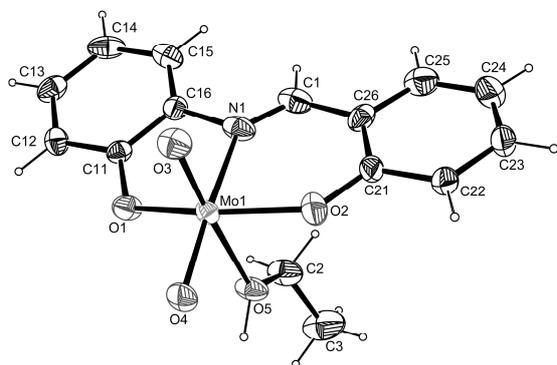


Figure 2. Ortep view of MoO<sub>2</sub>(SAP)(EtOH)

Table 2 – Relevant crystallographic distances (Å) and angles (°) of MoO<sub>2</sub>(SAP)(EtOH)

Bond lengths	(Å)	Angles (°)	
Mo(1)–O(3)	1.689(3)	O(3)–Mo(1)–O(4)	106.01(15)
Mo(1)–O(4)	1.695(3)	O(3)–Mo(1)–O(2)	100.35(15)
Mo(1)–O(1)	1.972(3)	O(4)–Mo(1)–O(2)	101.68(14)
Mo(1)–O(2)	1.914(3)	O(3)–Mo(1)–O(1)	97.33(14)
Mo(1)–O(5)	2.370(3)	O(4)–Mo(1)–O(1)	96.02(13)
Mo(1)–N(1)	2.291(4)	O(2)–Mo(1)–O(1)	150.34(15)
C(1)–N(1)	1.216(5)	O(3)–Mo(1)–N(1)	91.74(14)
C(1)–C(26)	1.448(6)	O(4)–Mo(1)–N(1)	160.60(13)
C(2)–O(5)	1.415(5)	O(2)–Mo(1)–N(1)	82.29(14)
C(11)–O(1)	1.354(4)	O(1)–Mo(1)–N(1)	73.53(13)
C(16)–N(1)	1.507(5)	O(3)–Mo(1)–O(5)	172.97(13)
C(21)–O(2)	1.329(5)	O(4)–Mo(1)–O(5)	80.77(12)
		O(2)–Mo(1)–O(5)	79.75(13)
		O(1)–Mo(1)–O(5)	79.84(12)
		N(1)–Mo(1)–O(5)	81.30(11)

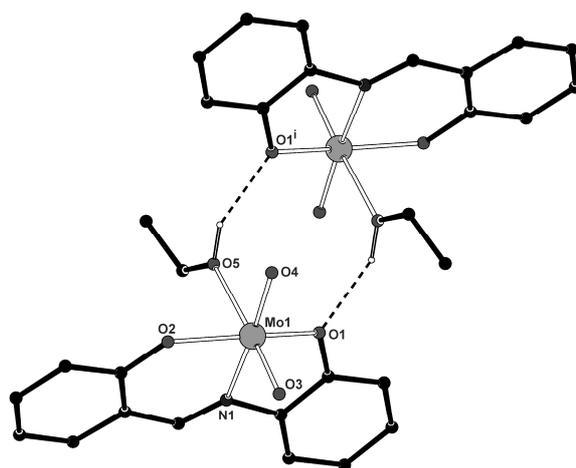


Figure 3. View of a pseudo-dimer formed through hydrogen bonding between two MoO<sub>2</sub>(SAP)(EtOH) molecules. Intermolecular hydrogen bonds are represented by dotted lines.

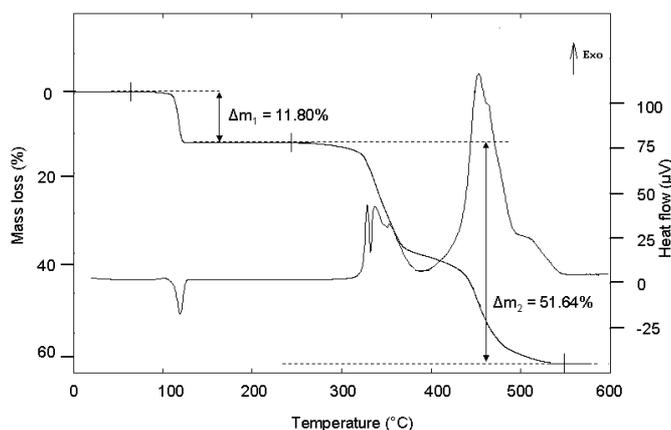


Figure 4. Thermogravimetric diagram of MoO<sub>2</sub>(SAP)(EtOH)

#### DFT study: relative stability of MoO<sub>2</sub>L(EtOH) and [MoO<sub>2</sub>(L)]<sub>2</sub> (L = SAP, SAE)

As stated above, the relative stabilization of the putative 5-coordinate MoO<sub>2</sub>L fragment by donor molecules D, forming MoO<sub>2</sub>L(D), or by dimerization to yield [MoO<sub>2</sub>L]<sub>2</sub> strongly depends on the nature of L and D [7,8]. With specific reference to the tridentate (O,N,O) ligands SAP and SAE, many stable MoO<sub>2</sub>L(D) compounds are known for both SAP (e.g. with D = MeOH, H<sub>2</sub>O, DMSO, amine, imidazoles, ethanol, SAEH<sub>2</sub> [7-10,12,14-16,19-21]) and SAE (D = DMF [22], MeOH [23,24], H<sub>2</sub>O [12], EtOH [13,25], SAEH<sub>2</sub> [8,26]). However, the SAE complexes show a greater tendency to dimerize, as indicated by the lower temperature for ethanol loss in the TGA [13].

In order to evaluate the influence of L on the relative preference of MoO<sub>2</sub>L(EtOH), and [MoO<sub>2</sub>L]<sub>2</sub>, we have carried out geometry optimizations and calculations of the thermodynamic parameters for both complexes as well as for the solvent-free intermediate MoO<sub>2</sub>L. It has to be

pointed out that these calculations refer to the ideal gas at 298 K; therefore, they do not take into account solvation effects. The energetic results of the calculations are summarized in Table 3 and depicted in Figure 5. The dimerization process (equation 1) is ideally broken into two steps, the first one being the ethanol decooordination to yield the 5-coordinate MoO<sub>2</sub>L fragment (equation 2) and the second being dimerization of the latter (equation 3).

Table 3 – Calculated enthalpy changes (in kcal mol<sup>-1</sup>) for the SAP and SAE systems

	L = SAP	L = SAE
$\Delta H^a$	+9.72	+6.27
$\Delta H_{decoordination}^b$	+9.70	+10.96
$\Delta H_{dimerisation}^c$	-9.69	-15.66

<sup>a</sup>Enthalpy change associated to reaction 1. <sup>b</sup>Enthalpy change associated to reaction 2. <sup>c</sup>Enthalpy change associated to reaction 3.

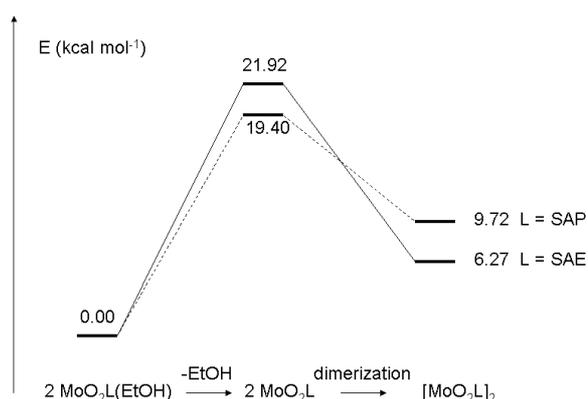
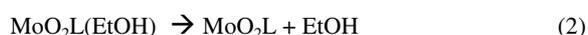
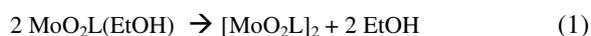


Figure 5. Enthalpy diagram for the conversion of MoO<sub>2</sub>L(EtOH) to [MoO<sub>2</sub>L]<sub>2</sub> in the gas phase (L = SAP, SAE).

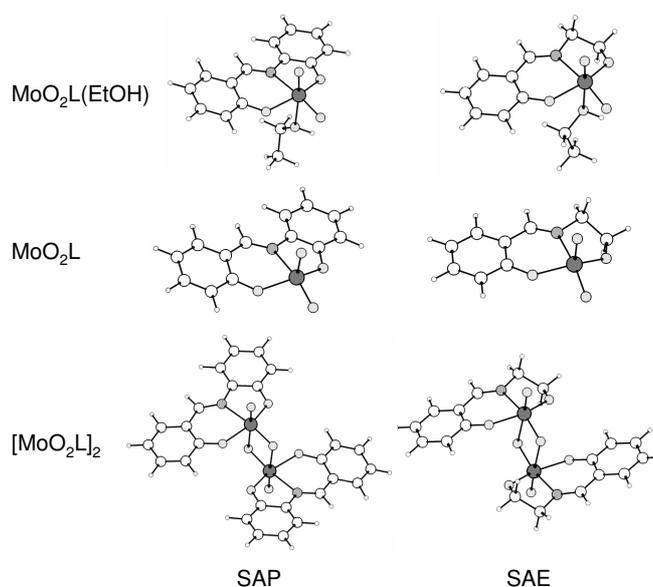


Figure 6. Optimized geometries of the MoO<sub>2</sub>L(EtOH), MoO<sub>2</sub>L and [MoO<sub>2</sub>L]<sub>2</sub> systems (L = SAP, SAE).

The total energy of the reaction in the gas phase for both ligands is qualitatively coherent with the experimental observations. The enthalpy change is in favour of the mononuclear ethanol-stabilized complex MoO<sub>2</sub>L(EtOH) in both cases, but more so for the SAP system. Examination of each separate step shows that the SAE system favors the 6-coordinate species, both the EtOH adduct and the dimer, relative to the mononuclear MoO<sub>2</sub>L fragment to a greater extent than the SAP system. However, whereas ethanol coordination is only mildly more exothermic, dimerization is more exothermic for SAE.

We have analyzed the optimized geometries (shown in Figure 6 with selected bond distances and angles collected in Table 4) more in detail in an attempt to pinpoint the cause of this energetic preference, but no clear factor, electronic or steric, seems to emerge from this analysis. The energy differences are only subtle, thus this analysis is not devoid of ambiguity. The most evident structural difference is the Mo-O (EtOH) distance, which is more than 0.1 Å longer in the SAE derivative, in apparent contradiction with the more favourable binding enthalpy. One conclusion that appears quite certain is that EtOH on one side and dimerization on the other side do not greatly perturb the coordination

Table 4 – Selected bond distances (Å) and angles (°) of the DFT optimized geometries

parameter	L = SAP			L = SAE		
	MoO <sub>2</sub> L(EtOH)	MoO <sub>2</sub> L	[MoO <sub>2</sub> L] <sub>2</sub>	MoO <sub>2</sub> L(EtOH)	MoO <sub>2</sub> L	[MoO <sub>2</sub> L] <sub>2</sub>
Mo=O <sub>ax</sub>	1.696	1.696	1.692	1.698	1.699	1.695
Mo=O <sub>eq</sub>	1.703	1.696	1.741	1.712	1.700	1.755
Mo-O (EtOH)	2.491	-	2.470	2.608	-	2.436
Mo-OPh1	1.985	1.963	1.949	1.984	1.970	1.967
Mo-OPh2	1.967	1.956	1.960	-	-	-
Mo-OCH <sub>2</sub> CH <sub>2</sub>	-	-	-	1.932	1.924	1.921
Mo-N	2.348	2.345	2.309	2.319	2.322	2.290
O=Mo=O	107.5	109.5	108.1	107.4	108.5	106.8
O <sub>ax</sub> -Mo-O(trans)	174.2	-	176.6	175.3	-	176.7
O(L)-Mo-O'(L)	145.8	138.3	149.6	145.9	136.5	150.7
N-Mo=O <sub>eq</sub>	159.1	152.9	154.4	156.1	155.4	151.7

geometry of the MoO<sub>2</sub>L moiety, in agreement with the small energy changes associated to these interactions.

## Conclusions

The X-ray structure of MoO<sub>2</sub>(SAP)(EtOH) is reported here for the first time. The energetic preference between mononuclear MoO<sub>2</sub>L(EtOH) and dinuclear [MoO<sub>2</sub>L]<sub>2</sub> has been studied by DFT in the gas phase for L = SAP and SAE. The greater propensity of the SAE system to yield the dinuclear product is reproduced by the calculations.

## Experimental Section

**Materials.** All experiments were carried out in air. Absolute ethanol and distilled water were used as solvents. MoO<sub>2</sub>(acac)<sub>2</sub> was purchased (Aldrich) and stored under a nitrogen atmosphere before use. MoO<sub>2</sub>(SAP)(EtOH) was obtained according to the literature procedures.[7]

**IR spectra.** Infrared spectra were recorded on KBr pellets at room temperature with a Mattson Genesis II FTIR spectrometer.

**TGA measurements.** The thermogravimetric analysis was performed on a SETARAM TGA 92-16.18 thermal analyzer. The sample was placed into a nickel/platinum alloy crucible and heated at 0.83 K s<sup>-1</sup> in a reconstituted air flow from 20°C to 600°C. An empty crucible was used as a reference.

**Synthesis of SAPH<sub>2</sub>.** Compound SAPH<sub>2</sub> was obtained by mixing 1.1 mL (10 mmol) of salicylaldehyde and 1.09 g (10 mmol) of *o*-aminophenol in 30 mL of distilled water. The mixture was stirred for two hours at room temperature yielding a red precipitate. The compound was separated by filtration, dried and recrystallized from ethanol. The red solid (61%) was then filtered off and dried. The purity was checked by IR and NMR spectroscopy.

**Crystallization of MoO<sub>2</sub>(SAP)(EtOH).** The complex was synthesized using the know procedures using MoO<sub>2</sub>(acac)<sub>2</sub> and SAPH<sub>2</sub> in boiling ethanol.[7] The crude precipitate was separated by filtration and recrystallized three times with hot ethanol, yielding orange crystals. The IR and NMR properties corresponded with those previously reported. [7, 12]

**Synthesis of [MoO<sub>2</sub>(SAP)]<sub>2</sub>.** Several ways can be used for the obtention of [MoO<sub>2</sub>(SAP)]<sub>2</sub>. The compound can be prepared by heating under vacuum or by letting the crystals of MoO<sub>2</sub>(SAP)(EtOH) stand in air for a long period [7,11]. The orange crystals turn to the brown color of [MoO<sub>2</sub>(SAP)]<sub>2</sub>. IR (cm<sup>-1</sup>, KBr pellets): 941 (Mo=O), 820 (Mo-O-Mo). TGA (20-600°C, 0.83 °C/min) Δm<sub>exp</sub> = 58.57% (Δm<sub>theo</sub> = 57.55%).

### Computational details.

The geometries of all species under investigation were optimized without any symmetry constraint with the Gaussian 03 [27] program suite. The input geometries were adapted from the X-ray structures of MoO<sub>2</sub>(SAP)(EtOH) (reported here) and [MoO<sub>2</sub>(SAE)]<sub>2</sub> [8]. The calculations used the standard B3LYP three-parameter functional, in conjunction with the 6-31G\*\* basis set for C, H, N and O atoms and with the CEP-31G\* basis set for Mo. All optimized geometries were confirmed to be local minima by frequency analyses, which were also used to derive the thermochemical parameters at 298 K according to the standard ideal gas approximation. (Optimized cartesian coordinates are available as supplementary material from the author)

## X-ray crystallography

A single crystal of compound MoO<sub>2</sub>(SAP)(EtOH) was mounted under inert perfluoropolyether on the tip of a glass fibre and cooled in the cryostream of a Bruker APEXII-II diffractometer. Data were collected using the monochromatic MoKα radiation (λ= 0.71073). The structure was solved by direct methods (SIR97) [28] and refined by least-squares procedures on *F*<sup>2</sup> using SHELXL-97.[29] All H atoms attached to carbon were introduced in idealised positions and treated as riding models in the calculations. The drawing of the molecule was realised with the help of ORTEP3. [30] Crystal data and refinement parameters are shown in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 721853. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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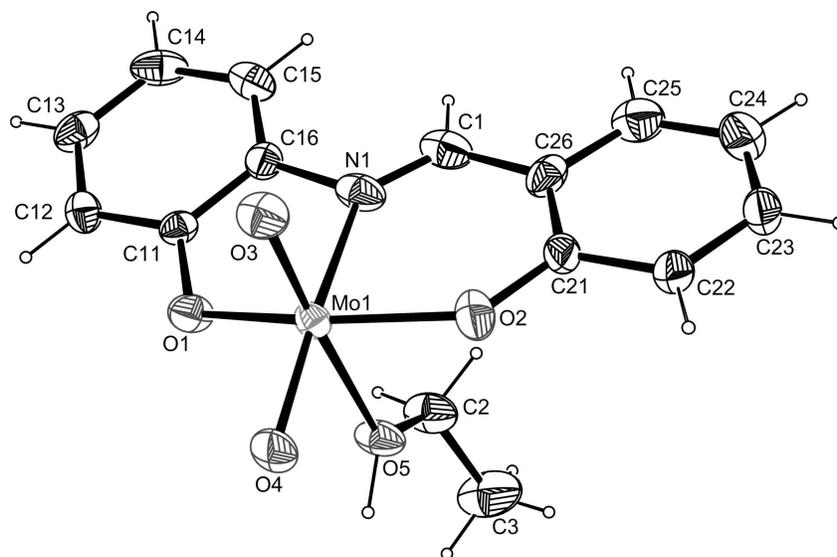


Figure 2. Ortep view of MoO<sub>2</sub>(SAP)(EtOH)  
120x80mm (600 x 600 DPI)

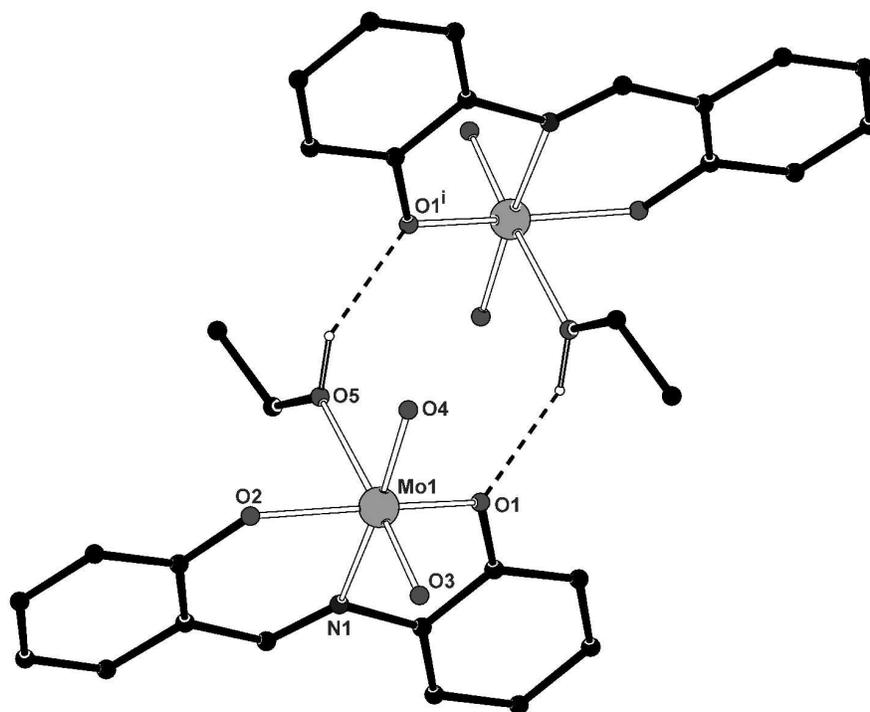


Figure 3. View of a pseudo-dimer formed through hydrogen bonding between two  $\text{MoO}_2(\text{SAP})(\text{EtOH})$  molecules. Intermolecular hydrogen bonds are represented by dotted lines.  
138x102mm (600 x 600 DPI)

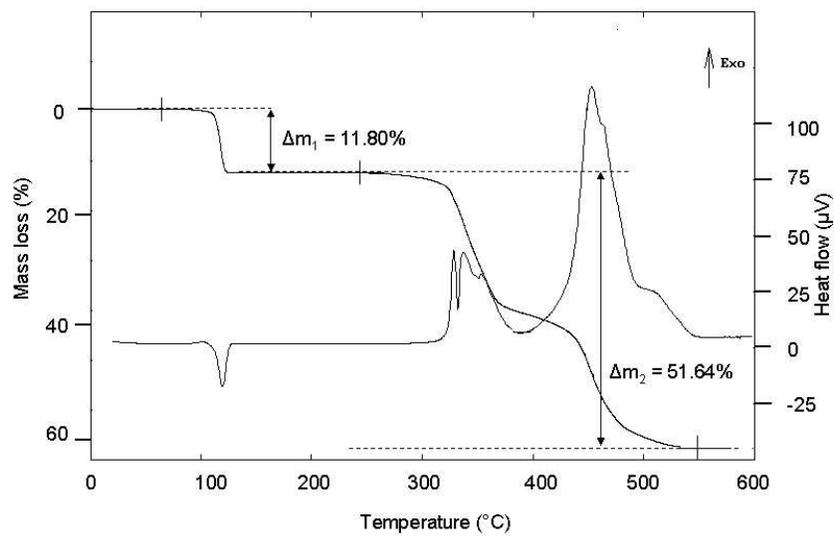


Figure 4. Thermogravimetric diagram of MoO<sub>2</sub>(SAP)(EtOH)  
254x190mm (96 x 96 DPI)

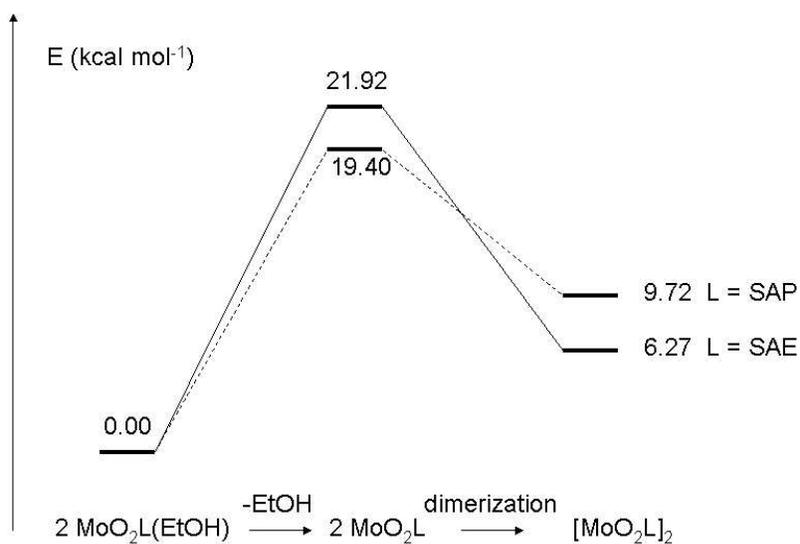


Figure 5. Enthalpy diagram for the conversion of MoO<sub>2</sub>L(EtOH) to [MoO<sub>2</sub>L]<sub>2</sub> in the gas phase (L = SAP, SAE).  
254x190mm (96 x 96 DPI)