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REACTIVITY OF α–BENZOIN OXIME WITH MOLYBDENUM(VI)

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ABSTRACT

In this work, we have presented various aspects of the reactivity of α–benzoin oxime with molybdenum(VI) based on the pH of the aqueous metal ion solution and the ligand/metal ratio. The reactivity of an ethanolic solution of α–benzoin oxime with an aqueous solution of molybdenum in the oxidation state VI was investigated at two pH values (1 and 2.5) and for different values of the ligand/metal ratio. Depending on the experimental conditions, the reaction of α–benzoin oxime (H_2L^1) ($C_6H_5(CHOH)$-$(C{=}NOH)C_6H_5$) with molybdenum(VI) leads to the formation of various complexes:
(1) A white monomeric coordination complex of the formula $[MoO_2(HL^1)_2].H_2O$. (2) A white dimeric coordination complex of the formula $Mo_2O_5(HL^2)_2(L^2)_2].H_2O$ in which L^2 is the deprotonated oxidized form of α–benzoin oxime, $C_6H_5(C{=}O)(C{=}NO)C_6H_5$. (3) A white dimeric coordination complex of the formula $[Mo_2O_5(L^2)_2(HL^3)_2]$ in which HL^3 is the hydrolyzed form of α–benzoin oxime, $C_6H_5(C{=}O)(CHOH)C_6H_5$.

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INTRODUCTION

The bibliography shows unanimous indications on the diversity of topologic, electronic, catalytic and specific biological properties of the oxomolybdenum(VI) ion. They were exploited in several applications[1-5]. One of the great assets of this element is the richness of its chemistry in water. Depending on the pH of the aqueous solution and the molybdenum(VI) concentration, we may distinguish cationic species such as MoO_2^{2+}, $Mo_2O_4^{4+}$, $Mo_2O_5^{2+}$, $HMo_2O_6^{+}$ whose coordination chemistry has been widely related and anionic species with variable degrees of condensation[6-9], such as $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4}$ or $H_3Mo_7O_{24}^{3-}$. Slaouti *et al.* have recently shown that the reaction of dimethylglyoxime (DMG) with molybdenum(VI), in well defined conditions of pH and concentration, leads to the adduct[10] $Mo_7O_{24}H_2(NH_4)(H_2L^3)_{10}.10H_2O$. This compound results from interactions between the acidic protons of the dioxime and the basic oxygens of the polyanion. Recently, studies on the reactivity of α–benzoin oxime in ethanolic solution with respect to vanadium in the oxidation states V, IV, III, II and nickel salts have been published[11,12].

The key features of this reactivity have been widely described. We have followed up this work by reacting this oxime with aqueous solutions of molybdenum in its highest oxidation state. The obtained results show that the pH of the aqueous solutions and the metal ion concentration are the preponderant parameters of the molybdenum(VI) redox and acidic properties which induce oxidation and hydrolysis of α–benzoin oxime, respectively. Based on the physical and chemical data (elemental analyses, UV–Visible, IR, ^1H and ^{95}Mo NMR, EPR, magnetic measurements, cyclic voltammetry, coulometry and mass spectrometry) the structures of the obtained complexes have been evaluated.

EXPERIMENTAL

Reagents and General Procedures

The reagents and solvents used were all pure Fluka for analysis products. The initial ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ concentration of the aqueous solutions was in the range 5×10^{-3}–5×10^{-1} M and those of α–benzoin oxime in ethanolic were in the range of 5×10^{-1}–1 M. All reactions were performed at room temperature by adding the ethanolic solution of the ligand to the aqueous molybdenum salt solution. The pH of the aqueous solution was previously adjusted. The ligand/metal ratio was varied in the range of 2–10. All obtained coordination complexes were filtered and washed with a mixture of water–ethanol (50–50 v/v).

Analytical and Physical Measurements

The elemental microanalyses and mass spectra (electrospray method) were carried out at the Central Service of Analysis of CNRS Solaize (France) on a JMS-D-100 mass spectrograph. Melting points were measured using an Electrothermal Buchi 512 melting point apparatus. The conductometric measurments were carried out with a CD 810 Tacussel conductivitymeter. The IR spectra were recorded on a FTS-7 Biorad Fourier Transform infrared spectrometer using KBr disks. The ^1H NMR spectra in $CDCl_3$ were recorded at 295 K on a Bruker AM 300 spectrometer with TMS as reference. The ^{95}Mo NMR spectra in DMSO were also recorded at 295 K on the same spectrometer with MoO_2Cl_2 as external reference. The electronic absorption spectra in DMSO solution were recorded on a Perkin Elmer Lambda 9 spectrometer using Suprasil cells. Magnetic susceptibilities were obtained at room temperature with a B-SU10 Bruker magnetic balance using $Hg[Co(SCN)_4]$ as paramagnetic reference; diamagnetic corrections were made using Pascal's constants. ESR spectra of paramagnetic compounds were recorded at room temperature and at liquid helium temperature with a Bruker ER 200 spectrometer. Cyclic voltammetry was performed with Tacussel equipment comprised of a Tacussel PRT 24-1 potentiostat and a GSATP generator. The physical properties and the elemental analyses of the complexes are summarized in Table I.

Preparation of Compounds

Complex (1). To 10 mmoles (2.273 g) of α–benzoin oxime (H_2L^1) dissolved in 20 mL of ethanol, was added a solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ (1 mmole, 1.236 g) in 20 mL of water. The pH of the aqueous solution was previously adjusted to 2.5 with a few drops of concentrated sulfuric acid. A white precipitate (0.478 g, 80 %) was formed immediately. This complex is insoluble in water but soluble in most organic solvents. It

Table I. Analytical Data and Conductance Values of the Complexes (in DMSO).

No	Complexes	Empirical Formula (molecular Weight) g/mole Found (calculated)	Colour	Yield %	M.p. ° C	% M	% C	% H	%N	Molar conductance (ohm^{-1} cm^{2} mol^{-1})
						Found (calculated)				
(1)	$MoO_2(HL^1)_2.H_2O$	$C_{28}H_{26}MoN_2O_7$ 598.94 (597.94)	White	80	150	15.99 (16.01)	56.05 (56.19)	04.63 (04.68)	04.32 (04.35)	35.72
(2)	$Mo_2O_5(HL^2)_2(L^2)_2.H_2O$	$C_{56}H_{44}Mo_2N_4O_{14}$ 1188.88 (1187.88)	White With blue Traces	80	180	16.11 (16.15)	56.55 (56.57)	03.65 (03.70)	04.69 (04.71)	50.49
(3)	$Mo_2O_5(HL^3)_2(L^2)_2$	$C_{56}H_{44}Mo_2N_2O_{13}$ 1144.88 (1143.88)	White	70	183	16.73 (16.77)	58.71 (58.74)	03.80 (03.85)	02.40 (02.45	34.32

is a non-electrolyte and diamagnetic. The elemental analyses and physical characterization data suggest the empirical formula: $C_{28}H_{26}MoN_2O_7$ which corresponds to $MoO_2(HL^1)_2.H_2O$.

Complex (2). To 20 mmoles (4.545 g) of α–benzoin oxime dissolved in 20 mL of ethanol were added 20 mL of an aqueous solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ (10 mmoles, 12.36 g). Previous to addition to the ligand, the pH of the aqueous solution has been adjusted to 2.5 with concentrated sulfuric acid. A white precipitate with blue traces (4.752 g, 80 %) was formed. It is insoluble in water but soluble in most organic solvents. It is slightly paramagnetic and a non–electrolyte. The elemental analyses and the physical characterization suggest the empirical formula $C_{56}H_{44}Mo_2N_4O_{14}$ which corresponds to $[Mo_2O_5(L^2)_2(HL^2)_2].H_2O$ where L^2 is the deprotonated oxidized form of α–benzoin oxime.

Complex (3). To 10 mmoles (2.273 g) of α–benzoin oxime dissolved in 20 mL of ethanol were added 20 mL of an aqueous solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ (5 mmoles, 6.179 g). The pH of the molybdenum solution was adjusted to 1 before addition to the ligand. A white precipitate (2.002 g, 70 %) was formed. This coordination complex is insoluble in water and highly soluble in DMF and DMSO. It is a non–electrolyte and a diamagnetic compound. The empirical formula is $C_{56}H_{44}Mo_2N_2O_{13}$ and the proposed formulation is $Mo_2O_5(L^2)_2(HL^3)_2$, where HL^3 is the hydrolyzed form of α–benzoin oxime.

RESULTS AND DISCUSSION

In our framework, we want to highlight a correlation effect between the pH, the concentration on molybdenum(VI) as well as its acidic and redox properties which implicitely induce oxidation and hydrolysis of α–benzoin oxime. Thus, under the given experimental conditions, the reaction of α–benzoin oxime with molybdenum(VI) leads to three types of complexes.

– The monomeric coordination Complex (1) at pH = 2.5 for a ligand/metal ratio = 10.

– The dimeric Complex (2) at pH = 2.5 for a ligand/metal ratio = 2.

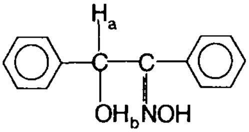
-The second dimeric Complex (**3**) at pH = 1 for the same ligand/metal ratio but at a lower metal ion concentration.

The formation of Complex (**2**) is accompanied by the appearance of few blue grains attributable to a Mo(V) coordination compound which is identified by UV-Visible, ESR and magnetic studies.

Complex (**1**)

The elemental analyses on one hand and the mass spectrum on the other hand with a peak at m/z = 599.94 g/mol (calc. 597.94 g/mol) allows us to conclude that monomer $MoO_2(HL^1)_2.H_2O$ was formed according to the following reaction of eq (1):

$$Mo^{6+} + 2\,H_2L^1 \xrightarrow{H_2O} Mo(VI)O_2(HL^1)_2.H_2O + 2\,H^+ + 2\,e^- \quad (1)$$



H_2L^1

Its IR spectrum, when compared with that of α–benzoin oxime (H_2L^1) clearly reveals the presence of hydration water and the hydroxylic group of the oxime function between 3600 and 3080 cm^{-1}. The disappearance of the proton of the hydroxyl group of H_2L^1 is due to the coordination of the α–benzoin oxime by the oxygen of this group after its deprotonation. The stretching vibration bands ν(C=N) and ν(N–O) shifted by 10 and 5 cm^{-1} towards lower wave numbers, respectively, suggesting the coordination of the ligand to the metal through the nitrogen of the oxime function. The two very intense bands of equal intensity observed at 935 and 910 cm^{-1} are assigned to the stretching vibration[13-15] of *cis*-MoO_2^{2+}. This domain of energy is well situated in the frequency range of molybdenum(VI) complexes in an oxygen and nitrogen environment. Finally, two new bands appeared in the range of 400–500 cm^{-1} (Table II) confirming the coordination of the deprotonated ligand (HL^1) to the metal through the phenelic oxygen

Table II. Infrared Spectral Data (in cm^{-1}) of the Complexes (KBr Discs).

Compounds	H_2O	H_{inter}	OH_{intra}	C=O	C=N	N-O	C-O	M=O	M-O-M	M-O	M-N
H_2L^1	—	3380 m	3243 m	—	1491 str	1242 str	986 m	—	—	—	—
HL^2	—	3350 str	3198 str	1678 str	1490 str	1240 m	—	—	—	—	—
HL^3	—	3442 m	3386 m	1680 str	—	—	980 str	—	—	—	—
Complex (1)	3600 sh (w)	—	3110 str	—	1489 str	1235 m	940 m	955 m 902 m	—	590 w	489 w
Complex (2)	—	—	3309 m	—	1491 str	1239 str	944 m	990 m 908 m	767 m 715 m	570 w	486 w 454 w
Complex (3)	—	—	3175 m	1685_f str 1646_c m	—	—	978 m	928 m 908 m	720 m 696 m	569 w 550 w 481 w	—

m: medium; str: strong; w: weak; f: free; c: coordinated

Table III. ^{1}H NMR Data (in ppm) and Coupling Constants in HZ.

Compounds	C_6H_5	OH	CH
H_2L^1	7.1-7.3 (10H, m)	5.58 (1H, d) 5.4 Hz	3.2 (1H, d) 5.4 Hz
HL^2	7.29-8.03 (10H, m)	—	—
HL^3	7.3-7.93 (10H, m)	5.96 (1H, d) 5.35 Hz	4.58 (1H, d) 5.35 Hz
Complex (1)	7-7.4 (10H, m)	—	3.1 (1 H, s)
Complex (2)	7-7.73 (10H, m)	—	—
Complex (3)	7.09-7.79 (20H, m)	6.29 (1H, d) 5.3 Hz	4.88 (1H, d) 5.3 Hz

(ν(Mo-O) = 490 cm^{-1}) and the nitrogen of the oxime function[10,11] (ν(Mo-N) = 429 cm^{-1}) (Table II).

Comparison of the ^{1}H NMR spectrum of the ligand with that of complex (**1**) confirms the coordination of α-benzoin oxime. This spectrum displays a range of proton resonances of the phenyl groups in H_2L^1 between 7-7.4 ppm and a singlet around 3.1 ppm due to the resonnance of the proton (H_a-C-OH_b) (Table III). The disappearance of the H of the hydroxyl group of H_2L^1 is in agreement with the IR deductions. No chemical signal related to the hydroxylic group of the free oxime function was observed in the spectra of free ligand and Complex (**1**). This observation suggests rapid exchange with the solvent. The signal appearing around 1.5 ppm is due to the presence of traces of water in the solvent used ($CDCl_3$).

Since molybdenum(VI) has a d^0 configuration, the only observed absorption bands in the UV-Visible spectrum of the monomer $MoO_2(HL^1)_2.H_2O$ describe the

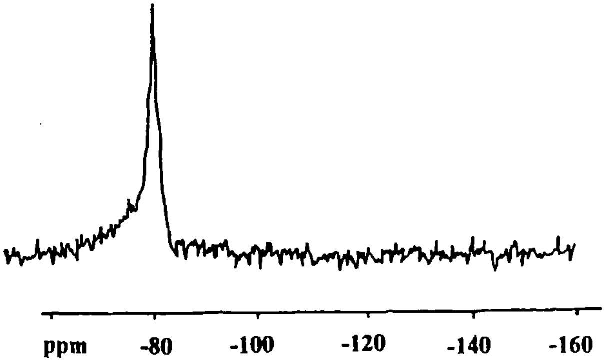


Fig. 1. ^{95}Mo NMR Spectrum of Complex (**1**).

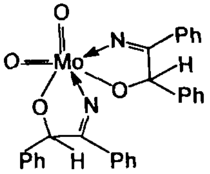


Fig. 2. Structure of Complex (**1**).

allowed intraligand $\pi - \pi^*$ transitions (λ = 250 nm, ε = 2.34×10^3 mol^{-1}.L.cm^{-1}), the ligand–metal charge transfer (λ = 270 nm, ε = 2.24×10^3 mol^{-1}.L.cm^{-1}) and the oxygen–metal transfer which is specific to the oxocation (λ = 275 nm, ε = 1.12×10^3 mol^{-1}.L.-cm^{-1}). This latter assignment takes in account recent work on molybdenum(VI) complexes[1,8,16].

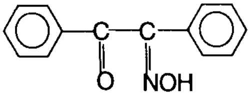
The ^{95}Mo NMR spectrum (Fig.1) presents only one line at –80 ppm. Its chemical shift conforms to those reported in the literature for molybdenum(VI) monomeric complexes in oxygen and nitrogen environments[10,17]. On the other hand, the line width exceeding 100 Hz confers to Complex (**1**) an octahedral symmetry[18,19]. On the basis of all the obtained results, the structure in Fig. 2 may be suggested for Complex (**1**).

The voltammogram of the complex $MoO_2(HL^1)_2.H_2O$ in DMSO–$LiClO_4$ presents a well resolved reversible reduction (ΔE = 0.405 V/SCE, Ia/Ic = 0.75) and is described by the following sequence: $Mo(VI) + 1e^- \longrightarrow Mo(V)$ (Ec = -0.28 V/SCE, Ea = +0.125 V/SCE). The reduction of Complex (**1**) at such positive potentials indicates the strong oxidant power of molybdenum.

Complex (2)

Under certain experimental conditions (pH = 1 and ligand/metal ratio = 2), the reaction between α–benzoin oxime and molybdenum(VI) has permitted the isolation of $[Mo_2O_5(HL^2)_2(L^2)_2.H_2O$ (eq 2). This compound has been identified by elemental analyses and mass spectra which show an isotopic mass at m/z = 1188.88 g/mol (calc. 1187.88 g/mol).

$$2\,Mo^{6+} + 4\,H_2L^1 \xrightarrow{H_2O} Mo(VI)_2O_5(HL^2)_2(L^2)_2.H_2O + 2\,H^+ + 2\,e^- \qquad (2)$$



HL^2

In the IR spectrum (Fig. 3) in the high energy range appears a shoulder and an intense band assigned, respectively, to the stretching vibrations of free water and an intramolecular band. The relatively intense free C=O stretching band vibration (1670 cm^{-1}) probably overlaps the band imputed to the deformation of ν(H...OH). The presence of two intense bands at 1670 and 1652 cm^{-1}, characteristic of free and coordinated carbonyl groups and the absence of the ν(C-O) vibration band which appeared at approximately 986 cm^{-1} in uncoordinated H_2L^1, must be the result of an oxidation of α–benzoin oxime to HL^2 by the oxygen of air. A similar reaction recently has been observed during a study of the reactivity of vanadium(V) with the same ligand[11]. On the other hand, the appearance of ν(C=N) and ν(N-O) frequencies is expected. Indeed, the oxidation of H_2L^1 $[C_6H_5(CHOH)(CNOH)C_6H_5]$ to HL^2 $[C_6H_5(CO)(CNOH)C_6H_5]$ leads to a gain of the stability and reinforcement of the two latter bands as a result of conjugation of the two double bonds.

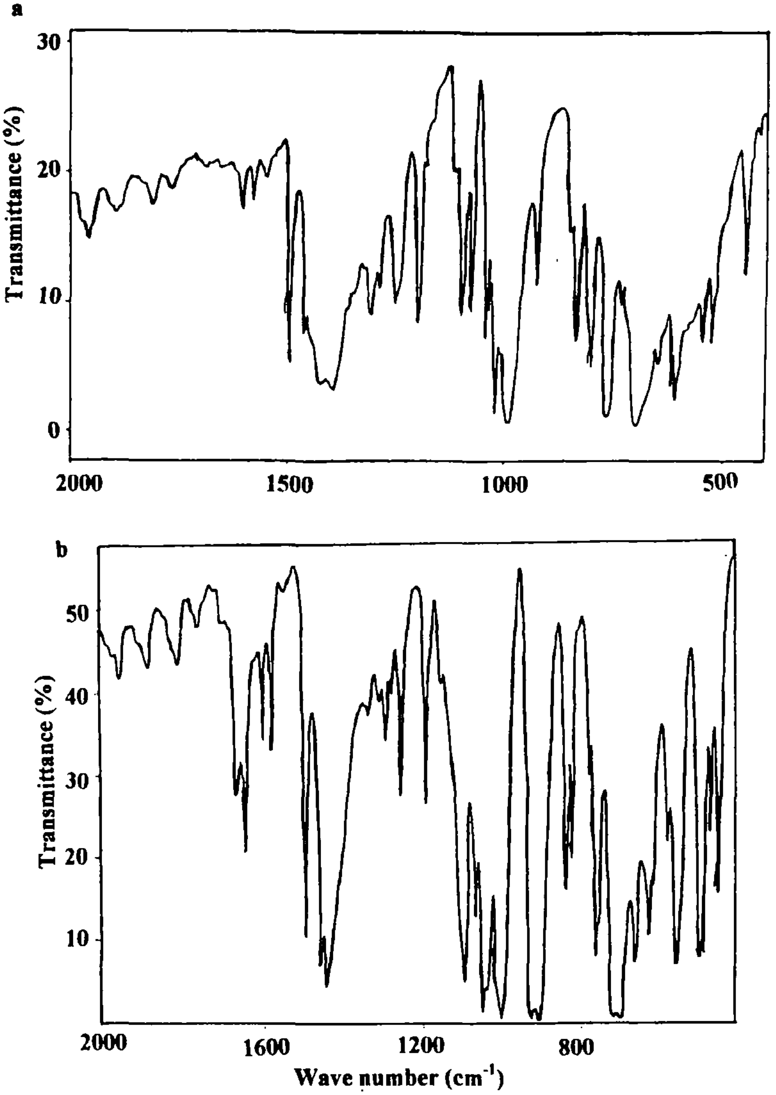
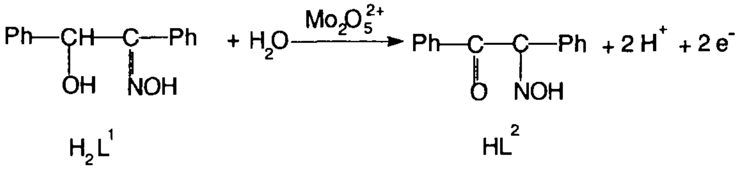


Fig. 3. IR Spectra of α-Benzoin Oxime (a) and Complex (**2**) (b).

Two strong absorptions of equal intensity, clearly resolved, are observed around 935 and 911 cm^{-1} assigned to the vibrations of MoO_2^{2+}, which are similar to Complex (**1**) and literature data[13,15]. The IR frequencies around 807 and 845 cm^{-1} are attributed to the antisymmetric and symmetric Mo-O-Mo vibrations[19,20]. This suggests a dimeric nature of Complex (**2**). The new bands appearing in the range of 600–400 cm^{-1} denote the coordination of HL^2 and its deprotonated form L^2 to the metal through the nitrogen of the oxime function and the oxygen of the carbonyl group. The IR observations (Table II) highlight the catalytic potential of $Mo_2O_5^{2+}$ in oxidation of the α–benzoin oxime in the presence of oxygen of air. The appropriate mechanism for this reaction is shown in eqs (3) and (4).



$$\underset{H_2L^1}{\mathrm{Ph{-}CH(OH){-}C(NOH){-}Ph}} + H_2O \xrightarrow{Mo_2O_5^{2+}} \underset{HL^2}{\mathrm{Ph{-}C(O){-}C(NOH){-}Ph}} + 2H^+ + 2e^- \qquad (3)$$

$$[\mathrm{Mo(VI)}]_2O_5^{2+} + 2H^+ + 2e^- \longrightarrow [\mathrm{Mo(V)}]_2O_4^{2+} + H_2O \xrightarrow{1/2\,O_2} [\mathrm{Mo(VI)}]_2O_5^{2+} \qquad (4)$$

The reduction of molybdenum(VI), illustrated by eq (2) is brought about the two electrons produced in eq (1). The Mo(V) species produced is reoxidized by the oxygen of air. Thus, the initial molybdenum valence, namely +VI, is regenerated.

The IR observations are in agreement with ^1H NMR results which confirm the oxidation of α–benzoin oxime (Table III). The integration of this spectrum suggests the presence of a multiplet between 7 and 7.73 ppm, a singlet at 11.38 ppm due to the resonance of ten phenolic protons and a strong hydrogen bond, respectively. The disappearance of the resonance of the protons (H_a and H_b) of H_2L^1 is compatible with the oxidation of the oxime. No signal due to the mobile proton of the oxime function of HL^2 has been observed. This absence suggests rapid exchange with $CDCl_3$.

The ^{95}Mo NMR spectrum in deuterated DMSO presents only one line at around –150 ppm with a line width of 350 Hz suggesting equivalent molybdenum atoms. The observed line width is in agreement with the octahedral symmetry of each molybdenum atom in the dimer. Indeed, we note a strong shielding of molybdenum in this compound compared with Complex (**1**) [18,19].

The electronic absorption spectrum exhibits a band at $\lambda = 255$ nm ($\varepsilon = 2.48 \times 10^4$ $mol^{-1}.L.cm^{-1}$) attributable to a $\pi - \pi^*$ transition; two shoulders at $\lambda = 275$ nm ($\varepsilon = 1.98 \times 10^4$ $mol^{-1}.L.cm^{-1}$) and $\lambda = 285$ nm ($\varepsilon = 9.15 \times 10^4$ $mol^{-1}.L.cm^{-1}$) assigned to ligand-metal and O-Mo charge transfer transitions and a band at $\lambda = 625$ nm ($\varepsilon = 1.93$ $mol^{-1}.L.cm^{-1}$) attributable to a d-d transition[19]. This latter result in conjunction with ESR and magnetic studies ($\mu = 0.27$ MB), confirm the existence of traces of molybdenum(V).

The EPR spectrum shows a well-resolved sextet hyperfine coupling pattern of the spin-active Mo nuclei ($I = 5/2$) with the impaired e^- ($I = 1/2$) and displays the features $g_0 = 1.932$ and $A_0 = 47.3$ Gauss. The most likely structure for this complex is illustrated in Fig. 4.

The voltammogram of the dimeric complex $Mo_2O_5(HL^2)_2(L^2)_2.H_2O$ (Fig. 5) exhibits two cathodic peaks at –0.2 and –0.32 V/SCE involving one electron for each electroreduction reaction[21].The appearance of an anodic wave at +0.145 V/SCE confirms the reversibility of the first system ($\Delta E = 0.345$ V/SCE, Ic/Ia = 0.77). The peaks can be attributed, respectively, to $Mo(VI) + 1e^- \longrightarrow Mo(V)$ ($Ec_1 = -1.12$ V/SCE, $Ea_1 = -1.2$V/SCE) and $Mo(VI) + 1e^- \longrightarrow Mo(V)$ ($Ec_2 = -1.55$ V/SCE). The weak waves appearing at –1.2 and –1.54 V/SCE confirm again the existence of traces of molybdenum(V) in Complex (**2**).

Complex (3)

Under the given experimental conditions, two synchronous reactions, catalyzed by molybdenum(VI), give rise to oxidation and hydrolysis of α–benzoin oxime.
The two resulting ligands HL^3 and L^2 have presented a similar chelating power towards $Mo_2O_5^{2+}$ species and lead to the precipitation of Complex (3) (eq 5).

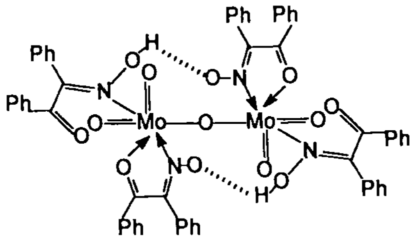


Fig. 4. Structure of Complex (**2**).

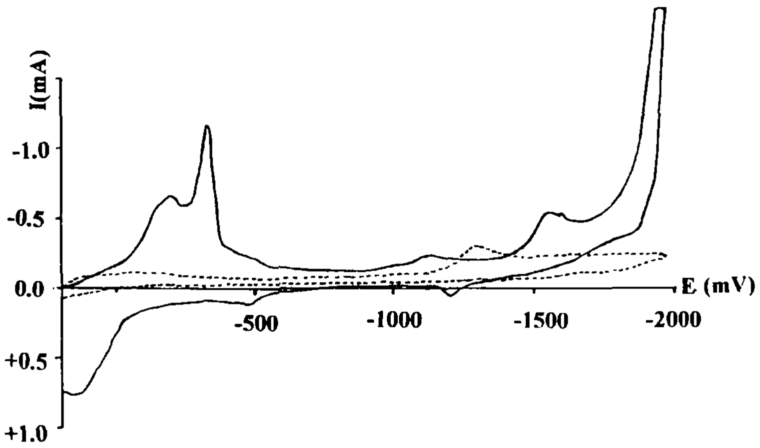
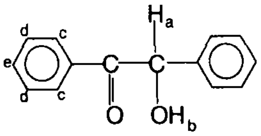


Fig. 5. Cyclic Voltammogram of Complex (**2**) in DMSO (V = 40 mVs^{-1}; 0.2 M $LiClO_4$). (---) blanck ; (—) [Mo] = 0.034 × 10^{-3} M.

$$2\,Mo^{6+} + 4\,H_2L^1 \longrightarrow Mo(VI)_2O_5(L^2)_2(HL^3)_2 + 2\,H^+ \qquad (5)$$



HL^3

The elemental analyses and mass spectrum which shows a peak at m/z = 1144.88 g/mol (calc. 1143.88 g/mol) corresponds exactly to the molecular mass of a dimeric complex of the formula: $[Mo_2O_5(HL^3)_2(L^2)_2]$.

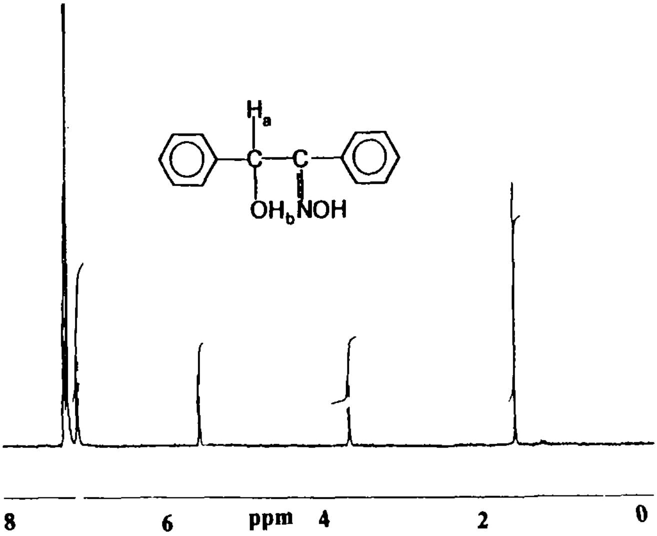
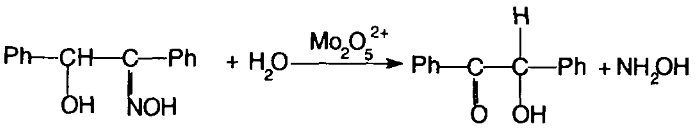


Fig. 6. ^{1}H NMR Spectrum of H_2L^1 in $CDCl_3$.

Its IR spectrum, compared with the one of Complex (**2**), reveals some similarity (Table II). Its shows an intramolecular band ν(OH) at 3166 cm^{-1} and a bathochromic shifting of the ν(C=N) and ν(N–O) frequencies as observed in Complex (**2**). It also shows two bands at 1673 and 1642 cm^{-1} that correspond to free and coordinated carbonyl groups, respectively. The existence of these latter bands and the nitrogen experimental microanalyses data (0%) confirm the oxidation (same mechanism as in Complex (**2**)) and hydrolysis of α–benzoin oxime. A similar reaction has been observed between vanadium(III) and α–benzoin oxime[11]. The oxidation product was identified by X-ray diffraction to be benzoin. The appropriate mechanism for hydrolysis is shown in eq (6) is:



$$Ph-CH(OH)-C(=NOH)-Ph + H_2O \xrightarrow{Mo_2O_5^{2+}} Ph-C(=O)-CH(OH)-Ph + NH_2OH \quad (6)$$

H_2L^1 HL^3

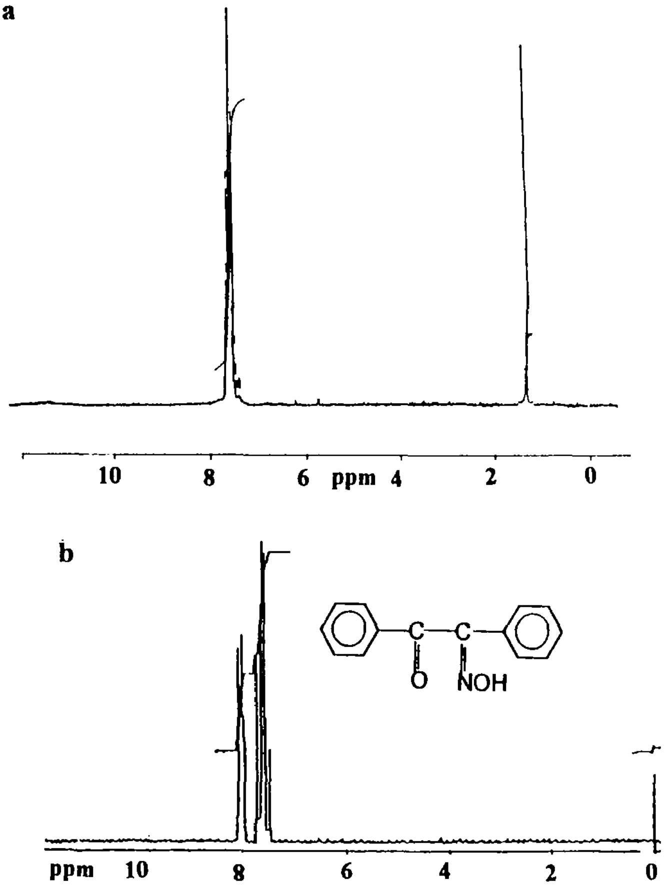


Fig. 7. ^1H NMR Spectrum of Complex (2) (a) and Simulation of HL^2 (b).

The two bands specific of MoO_2^{2+} vibrations are observed[13,15] around 902 and 931 cm^{-1}. Those of antisymmetric and symmetric Mo-O-Mo around 844 and 776 cm^{-1} according to literature data[19,20]. These confirm the dimeric nature of Complex (3). The bands appearing at 577, 441 and 484 cm^{-1} suggest a coordination of L^2 (by the oxygen of the carbonyl and the nitrogen of the free oxime function) and HL^3.

Furthermore, the ^1H NMR spectrum of this complex is equal to the superimposition of those of HL^3 and L^2 (Figs. 6, 7, 8 and 9). Its integration reveals the presence of a

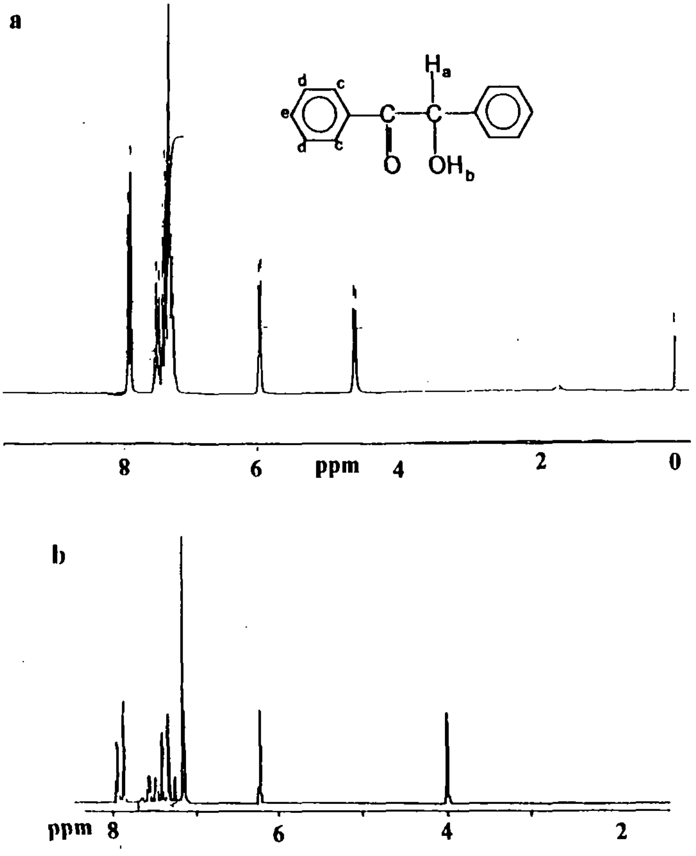


Fig. 8. ^1H NMR Spectrum of HL^3 in $CDCl_3$ (a) and Simulation of HL^3 (b).

strong hydrogen bond which appears as a singlet at 11.44 ppm. The multiplet in the range 7.09-7.79 ppm is due to the resonance of twenty phenyl protons. Two doublets resulting from coupling between the protons (H_a–COH_b) are observed around 4.88 and 6.29 ppm ($J^3 = 5.3$ Hz). In fact, the phenyl proton involved in a chelating hydrogen bond in Complex (3) doesn't undergo exchange with D_2O. The signal appearing around 1.5 ppm is due to the presence of traces of water in the solvent used. In conclusion, the intensity ratio of the four resonances observed in the ^1H NMR spectrum of $Mo_2O_5(HL^3)_2(L^2)_2$ shows that hydrolysed (HL^3) and oxidized (L^2) forms of the oxime

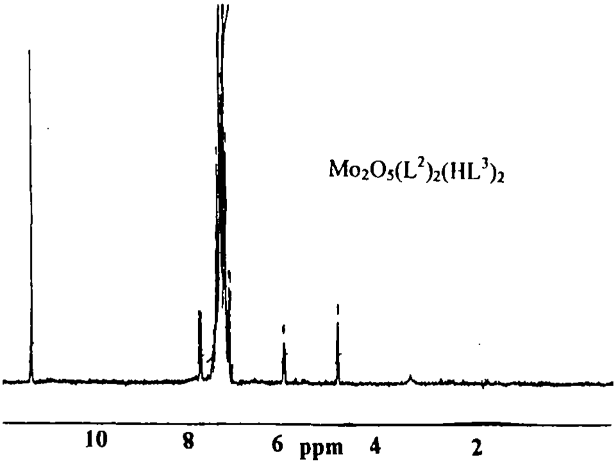


Fig. 9. ^{1}H NMR Spectrum of Complex (3) in $CDCl_3$.

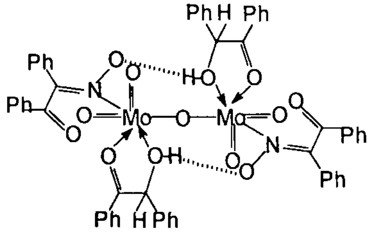


Fig. 10. Structure of Complex (3).

are formed in equal proportion (Table III). This dimeric compound (Complex (3)) also has been detected by ^{95}Mo NMR by its negative chemical shift (-125 ppm) due to the important electronic density around the donor sites of the ligands[22]. The observation of only one line (325 ppm) in ^{95}Mo NMR spectrum suggests equivalent molybdenum atoms.

The electronic absorption spectrum of Complex (3) is composed of a band at λ = 260 nm ($\varepsilon = 4.25\times10^4$ mol^{-1}.L.cm^{-1}) attributed to a $\pi-\pi^*$ transition and two shoulders at λ = 265 nm ($\varepsilon = 3.69\times10^4$ mol^{-1}.L.cm^{-1}) and λ = 295 nm ($\varepsilon = 2.23\times10^4$ mol^{-1}.L.cm^{-1})

assigned to a ligand-metal and O-Mo charge transfer transitions, respectively. This spectrum, as expected, does not show any d-d band, which is in accordance with the magnetic results.

The shape of the cyclic voltammogram of Complexes (**2**) and (**3**) is some what comparable. Complex (**3**) is reduced in two mono-electronic steps corresponding to the couples Mo(VI)/Mo(V) and Mo(VI)/Mo(V) (Ec_1 = - 0.08 V/SCE, Ec_2 = - 0.22 V/SCE). These potential values are in the range provided by similar dimeric complexes[14]. The two anodic peaks observed at Ea_1 = - 0.33 V/SCE and Ea_2 = - 0.46 V/SCE confirm the reversibility of the two systems (ΔE = - 0.25 V/SCE, Ia/Ic = 1.32, ΔE = - 0.24 V/SCE, Ia/Ic = 0.84).

The spectroscopic observations and elemental analyses results impose an octahedral coordination for each molybdenum atom. Thus, we propose the structure illustrated in Fig. 10. for Complex (**3**).

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