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TRANSITION-METAL COMPLEXES WITH HYDRAZIDES AND HYDRAZONES

7. Dioxomolybdenum(VI) complexes of salicylaldehyde *p*-hydroxybenzoylhydrazone and their thermal stability

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Abstract

Several new complexes of dioxomolybdenum(VI) of the general formula $[MoO_2(L)S]$, where *L* is the dianion of salicylaldehyde *p*-hydroxybenzoylhydrazone and *S* denotes H_2O, MeOH, py, PPh_3, DMSO or DMF, were synthesized and characterized by elemental analysis, electronic UV-VIS and IR spectra, thermal analysis, molar conductivity and magnetic susceptibility measurements. Salicylaldehyde *p*-hydroxybenzoylhydrazone participates in the coordination as a tridentate ligand with the ONO set of donor atoms. The complexes contain a *cis*-MoO_2 group and are of octahedral geometry. Complexes of the MoO_2L type were also prepared by synthesis in $CHCl_3$ solution and by isothermal heating of $[MoO_2(L)S]$ complexes. The MoO_2L complex synthesized in $CHCl_3$ solution has most probably a pentacoordinated structure while the complex obtained by isothermal heating of $[MoO_2(L)S]$ has a polymeric hexacoordinated structure.

Keywords: complexes

Introduction

Of the second transition series metals only molybdenum is an essential micronutrient for living systems such as plants, animals and microorganisms. Higher oxidation states are dominant in oxomolybdenum complexes which are components of a number of redox enzymes taking part in the biological fixation

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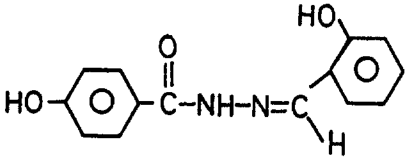
of nitrogen [1–3]. This paper deals with relatively simple dioxomolybdenum(VI) complexes with one coordination site in the trans-position to an oxo-oxygen, to which there may be attached various monodentate donors loosely bound to molybdenum, on account of which they can be easily replaced by various substrates. The functioning of enzymes is enabled by this easy substitution of the *trans*-ligand by substrate molecules [4]. These complexes were synthesized by using a planar tridentate ligand as part of the octahedral coordination sphere of molybdenum(VI). Taking into account the increasing interest in transition metal complexes of hydrazides and hydrazones because of their applications in medicine, analytical chemistry, in the synthesis of new heterogeneous catalysts for redox processes and in many other scientific and technological fields [5, 6], we have dedicated this paper to dioxomolybdenum(VI) complexes with salicylaldehyde *p*-hydroxybenzoylhydrazone (H_2L) as a tridentate ONO donor.

Experimental

All chemicals used were commercial products of analytical reagent grade. $MoO_2(acac)_2$ and H_2L were synthesized according to procedures reported in the literature [7, 8].



(H_2L)

C, H, N analyses were performed by standard micromethods at the Department of Instrumental Analysis of the Faculty of Chemistry, Belgrade University, using air dried substances. IR spectra were recorded on a Perkin-Elmer FT-IR 1726X spectrophotometer, using KBr pellet technique. The electronic spectra of MeOH solutions were recorded on a GBC 911A spectrophotometer. Molar conductivities of 1×10^{-3} mol dm^{-3} MeOH solutions were measured at room temperature with a Jenway-4009 conductivity meter. Thermogravimetric and DTA measurements were carried out on a Linseis derivatograph at a heating rate of 10°C min^{-1} in an air atmosphere, heated alumina being employed as standard. DSC curves were recorded on a DuPont 1090 thermal analyser in a hydrogen atmosphere up to 500°C. Magnetic susceptibilities were checked by the Faraday method at room temperature.

Synthesis of the complexes

$[MoO_2(L)MeOH]$

A solution of H_2L (1 mmol) in hot absolute methanol was mixed with the solution of $MoO_2(acac)_2$ (1 mmol) in hot absolute methanol and heated for

10 min. The precipitated silky, yellow-coloured crystalline product was filtered off and washed with MeOH. Yield: 75%.

$[MoO_2(L)H_2O]$

This complex was synthesized by the same procedure as already described, the only difference being the use of 80% methanol as solvent. Yield: 80%

$[MoO_2(L)py]$, $[MoO_2(L)PPh_3]$, $[MoO_2(L)DMF]$ and $[MoO_2(L)DMSO]$

To the hot methanolic solution of $MoO_2(acac)_2$ (1 mmol) and H_2L (1 mmol) was added under stirring 1 cm^3 of py, DMSO, DMF, and PPh_3, respectively. Heating was continued for additional 20 min, and then the solutions were left overnight to crystallize. The products obtained were washed with MeOH. Yields: 60–66%.

MoO_2L

$MoO_2(acac)_2$ (1 mmol) and H_2L (1 mmol) were homogenized in a mortar. The homogenized mixture was dissolved in hot chloroform and the solution was heated for 15 min. The product was filtered off and washed with methanol. Yield: 61%.

Results and discussion

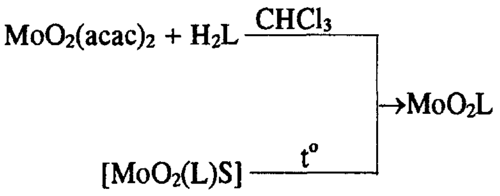
The reaction of $MoO_2(acac)_2$ with H_2L in a mole ratio of 1:1 in the presence of the appropriate monodentate donors *S*, gives rise to the following complex compounds:

$$MoO_2(acac)_2 + H_2L \xrightarrow{S} [MoO_2(L)S] + 2\ Hacac$$

$$S = MeOH,\ H_2O,\ py,\ DMSO,\ DMF\ or\ PPh_3$$

The deprotonation of H_2L is achieved by removal of the acetylacetonato anion which is a good proton acceptor. The non-electrolyte nature of the obtained complexes was confirmed by the low molar conductivities (λ_M= 2.2–4.3 $\Omega^{-1}cm^2\ mol^{-1}$). They are diamagnetic as expected for the $4d^0$ configuration for molybdenum(VI) species. In accordance with the $4d^0$ configuration, the absorptions appearing in the electronic spectra in the range 280–400 nm arise from intraligand and ligand–to–metal charge transfer transitions.

All complexes are yellow or orange crystalline substances (Table 1), soluble in MeOH, EtOH, py, DMF and $CHCl_3$, but insoluble in H_2O and C_6H_6. In $CHCl_3$ solution the reaction leads to the formation of MoO_2L. The latter type of complex was also obtained by heating $[MoO_2(L)S]$ at 105°C for two hours:



$$\left.\begin{array}{l} MoO_2(acac)_2 + H_2L \xrightarrow{CHCl_3} \\ \\ [MoO_2(L)S] \xrightarrow{t^o} \end{array}\right] \rightarrow MoO_2L$$

The complexes undergo substitution reactions of the type $[MoO_2(L)S]+S'=[MoO_2(L)S']+S$, where S and S' are different donor molecules. The addition of a small amount of water to an MeOH solution of $[MoO_2(L)MeOH]$, yields immediately $[MoO_2(L)H_2O]$. After addition of DMF to $[MoO_2(L)H_2O]$ in methanol, the crystalline $[MoO_2(L)DMF]$ precipitated. On the basis of experiments of this type a qualitative order of increasing strength of S binding can be proposed: $MeOH<H_2O<DMF<DMSO<py<PPh_3$. Strong binding of PPh_3 donor can be expected because of its π acceptor ability.

The donor sites of the ligand were identified on the basis of IR spectral data (Table 2). The IR spectrum of the free solid ligand H_2L exhibits a $\nu(C=O)$ vibration at 1640 cm^{-1}, pointing to its acylhydrazine form. The addition of a metal cation causes enolization of the acylhydrazine into an oxyazine form [9], whose

Table 1 Colour and elemental analysis of molybdenum(VI) complexes

Complex/Stoichiometry	Colour	Found(Calcd.)/%		
		C	H	N
$[MoO_2(L)MeOH]$	yellow	43.38	3.65	6.90
$C_{15}H_{14}O_6N_2Mo$		(43.49)	(3.41)	(6.76)
$[MoO_2(L)H_2O]$	yellow	41.99	3.30	7.20
$C_{14}H_{12}O_6N_2Mo$		(42.02)	(3.02)	(7.00)
$[MoO_2(L)py]$	orange	49.19	3.59	8.97
$C_{19}H_{15}O_5N_3Mo$		(49.47)	(3.28)	(9.11)
$[MoO_2(L)PPh_3]$	orange	59.21	3.80	4.39
$C_{32}H_{25}O_5N_2PMo$		(59.60)	(3.91)	(4.35)
$[MoO_2(L)DMSO]$	orange	41.82	3.07	5.79
$C_{16}H_{16}O_6N_2SMo$		(41.74)	(3.48)	(6.09)
$[MoO_2(L)DMF]$	orange	44.87	4.01	9.12
$C_{17}H_{17}O_6N_3Mo$		(45.13)	(3.76)	(9.29)
$MoO_2(L)$	orange	43.84	2.86	7.33
$C_{14}H_{10}O_5N_2Mo$		(44.00)	(2.64)	(7.31)

Table 2 Thermal analysis[a], IR and electronic spectral data of dioxomolybdenum(VI) complexes

$[MoO_2(L)S]$ S:	MeOH	H_2O	py	PPh_3	DMSO	DMF	$MoO_2(L)$[b]	$MoO_2(L)$[c]
T_i/°C	87	117	130		163	123		
T_f/°C	115	125	160		218	140		
Δm/% Found	7.0	3.9	16.7		17.3	16.4		
(Calcd.)	7.7	4.5	17.1		17.0	16.0		
IR/cm^{-1}								
ν(C=N)	1611	1611	1609	1619	1620	1613	1610	1612
ν(C–O)[d]	1235	1235	1260	1259	1260	1269	1235	1237
ν(C–O)[e]	1550	1550	1547	1545	1552	1552	1550	1548
ν(Mo=O)	935	934	932	941	939	936	935	925
	913	912	910	913	911	909	913	831
	896	896	893	903	900	892	896	
Selected S vibrations	3380[f]	3385[f]	620[g]		999[h]	1643[i]		
UV-VIS (nm)								
λ_{max}	400	398	323	320	323	325	397	380
	323	320	289	287	300	289	325	315

[a] T_i = initial temperature; T_f = final temperatures; [b] Formed in $CHCl_3$ solution; [c] Formed by isothermal heating; [d] enolic; [e] phenolic; [f] ν(O–H); [g] In-plane ring deformation; [h] ν(S=O); [i] ν(C=O).

stability is attributed to conjugation extended along the whole ligand molecule. A new band in the range 1235–1270 cm^{-1} appearing in the spectra of complexes corresponds to the enolic C–O bond. The ν(C=N) vibration occurring in the ligand spectrum at 1624 cm^{-1} is shifted in the spectra of complexes to lower energies by 5–15 cm^{-1}, suggesting the coordination of the azomethine nitrogen to molybdenum. This lowering is rather small, but indicative of coordination. On the other hand, it suggests how little this mode of vibration is affected by coordination [10]. Due to the partial double bond character of the phenolic C–O bond, the phenolic ν(C–O) stretching vibration is expected at higher energy in comparison to the enolic ν(C–O). The phenolic ν(C–O) band at 1535 cm^{-1} arising from the Schiff base is shifted towards higher energies by 10–15 cm^{-1}, which indicates the coordination of the phenolic oxygen [11, 12]. The ligand H_2L takes part in coordination as a dianion, formed by deprotonation of both the phenolic and enolic groups, as is apparent from the disappearance of the ν(O–H) and ν(N–H) bands in the spectra of $[MoO_2(L)py]$, $[MoO_2(L)DMSO]$ and $[MoO_2(L)PPh_3]$. Thus, the IR data are indicative of the tridentate, dibasic ONO donor behaviour of the ligand H_2L.

The $[MoO_2(L)S]$ complexes usually exhibit two strong bands in regions 950–910 and 875–914 cm^{-1} which are assigned as ν_s(O=Mo=O) and

ν_{as}(O=Mo=O) stretching vibrations respectively. In some cases these bands are split by ca. 15 cm^{-1} and this band splitting may be due to the crystal packing effect [13]. The [MoO$_2$(L)S] complexes described in this work, similarly to some other known MoO$_2$ species [14–17], exhibit three bands in the region 950–875 cm^{-1}. Replacement of *S* by *S'* does not significantly affect the energy difference between ν_s(O=Mo=O) and ν_{as}(O=Mo=O). The MoO$_2$L complex prepared by isothermal heating of [MoO$_2$(L)S] displays a characteristic strong vibration at 820 cm^{-1} which is absent in the spectra of [MoO$_2$(L)S] [14]. In most cases complexes of the MoO$_2$L type exhibit only a single stretching vibration at 930 cm^{-1} instead of the usual *cis*-MoO$_2$ doublet appearing in the spectra of [MoO$_2$(L)S]. This is the case with the MoO$_2$L complex obtained in this work, where the band at 925 cm^{-1} corresponds to the ν(Mo=O) vibration and that at 831 cm^{-1} to the weakened ν(Mo=O), present in the bridging $\mathrm{Mo}\text{---}\mathrm{O}\longrightarrow\mathrm{Mo}$ moiety. Hence, it may be concluded that MoO$_2$L obtained by isothermal heating of [MoO$_2$(L)S] has a polymeric octahedral chain-like structure (Fig. 1b). It should be mentioned that some complexes of this structure give rise as many as four bands in the region 945–820 cm^{-1} [17, 18]. The possibility of polymerization through a phenolic oxygen is less probable in view of the fact that the phenolic ν(C–O) band appears almost at the same frequency in both the MoO$_2$L and [MoO$_2$(L)S] types of complexes. Otherwise, the bridg-

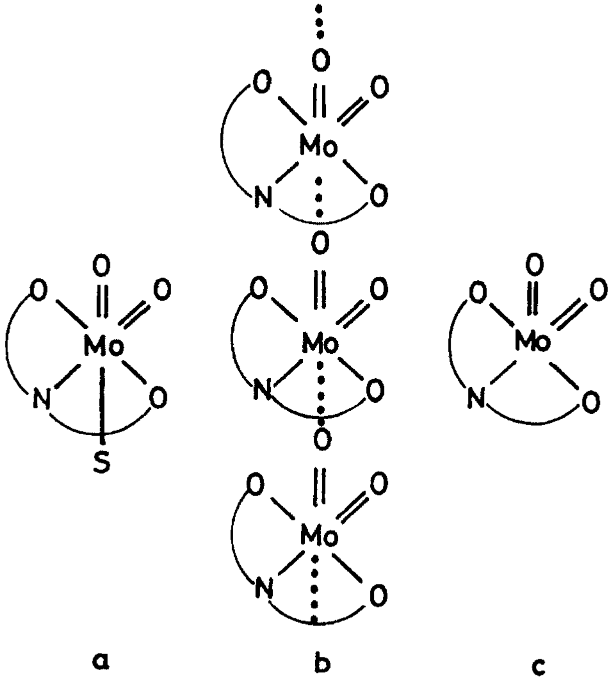


Fig. 1 Schematic presentation of [MoO$_2$(L)S] and MoO$_2$L structures

ing through phenolic oxygen would cause a substantial increase of the ν(C–O) stretching vibration band [14, 18, 19]. In the characteristic region 950–880 cm^{-1}, the IR spectrum of the MoO_2L complex obtained from a $CHCl_3$ solution is identical to the spectra of [MoO_2(L)S] complexes. Therefore, it may be assumed that it has a pentacoordinated structure (Fig. 1c).

The coordination of the monodentate donors *S* which occupy the sixth coordination site (Fig. 1a) is confirmed both by IR spectral data and the results of thermal analysis of [MoO_2(L)S] complexes (Table 2). The various *S* ligands are eliminated in endothermic processes (DTA in air), whereas the TG data confirm that the mass loss in each case is comparable with the loss of one *S* ligand. The temperature at which the desolvation of the [MoO_2(L)S] complex occurs (Table 2) gives evidence of the Mo–S bond strength, confirming the afore-proposed qualitative order of the strength of *S* binding. In the case of the [MoO_2(L)PPh_3] complex the endothermic peak was not registered, most probably due to the fact that PPh_3 is released only at higher temperatures, at which the decomposition of the tridentate ligand begins. Namely, at about 275°C the exothermal oxidation processes of H_2L decomposition begin, giving MoO_3 as the final product at 580–590°C.

Thermal investigations of the [MoO_2(L)py] complex and of both complexes of the MoO_2L type were carried out by recording DSC curves in the temperature interval 20–500°C in a hydrogen atmosphere. The DSC curves obtained in the temperature range 20–500°C in hydrogen and air atmosphere, respectively, as well as in closed cell, in the temperature range 20–300°C were identical, indicating that the hydrogen atmosphere has no effect on the decomposition mechanism. The DSC curve (in hydrogen) of the ligand (Fig. 2) points to its stability up to 266°C when melting, accompanied by decomposition (IR, TG), occurs, which was registered as an endothermic peak (DSC). Data obtained

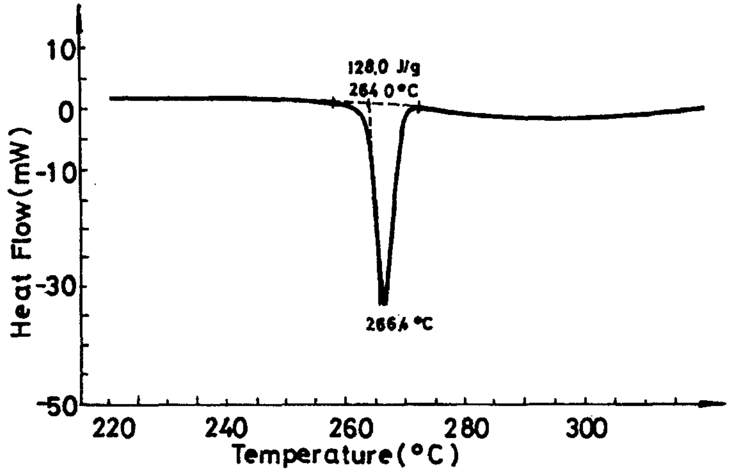


Fig. 2 DSC curve of H_2L (in hydrogen) at a heating rate of 20°C min^{-1}

from the DSC curves (Figs 3, 4 and 5) of the complexes [MoO_2(L)py], MoO_2L obtained from $CHCl_3$ and MoO_2L obtained by isothermal heating of [MoO_2(L)S] were correlated with structural characteristics derived from IR spectra. Namely, for the [MoO_2(L)py] complex and the MoO_2L complex obtained from $CHCl_3$ at 126.5 and 114°C, respectively, strong endothermic peak was found. This endothermal peak can be ascribed to the loss of py (disappearance of the band at 624 cm^{-1} in the case of [MoO_2(L)py]). On the basis of the IR spectra of these complexes at given temperatures (appearance of $\nu Mo — O \longrightarrow Mo$) at 830 cm^{-1}) after loss of py, a polymerization process occurs. The DSC curve of the MoO_2L complex, obtained by isothermal heating, shows an endothermic peak of low intensity at 128°C. (The IR spectrum of the complex treated at this temperature does not display any significant changes compared to the spectrum of the complex at room temperature.) These data also prove that MoO_2L obtained from $CHCl_3$ possesses a pentacoordinated structure, whereas MoO_2L obtained by heating of [MoO_2(L)S] has a polymeric octahedral structure. The exothermic peaks appearing on the DSC curves up to 300°C correspond to further structure ordering and are not accompanied by significant changes in the IR spectra. At temperatures above 300°C decomposition of the tridentate ligand begins, which is indicated by drastic changes in the IR spectra, whereas the DSC curves recorded in a hydrogen atmosphere as well as those of the hermetically closed sample, show two strong endothermic peaks. However, the DSC curves recorded in air within the same temperature interval

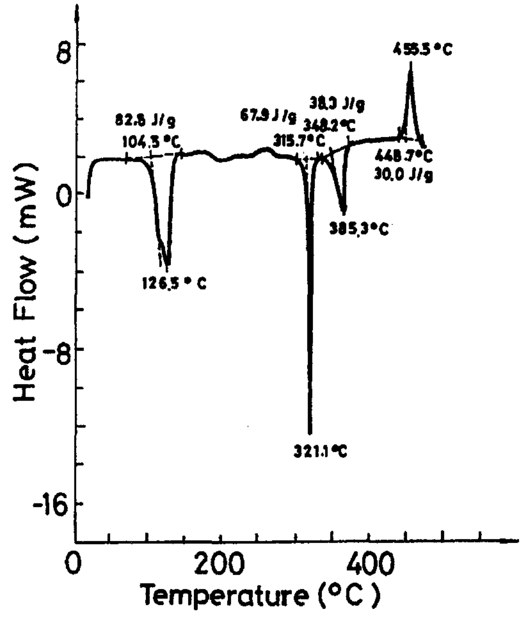


Fig. 3 DSC curve of [MoO_2(L)S] (in hydrogen) at a heating rate of 20°C min^{-1}

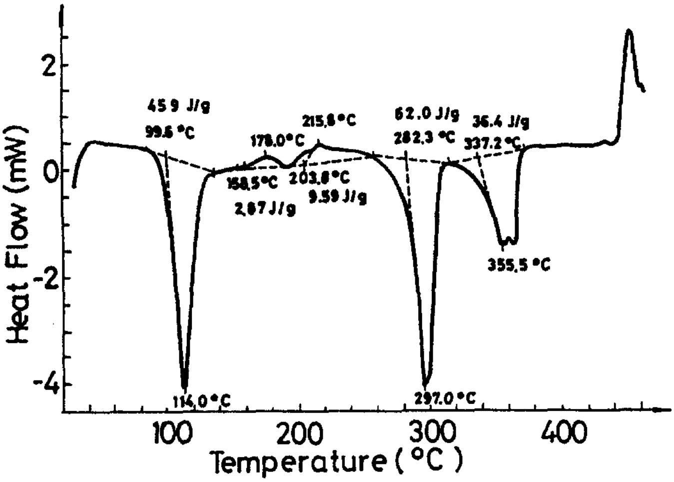


Fig. 4 DSC curve of MoO_2L obtained from $CHCl_3$ solution; in hydrogen at a heating rate of 20°C min^{-1}

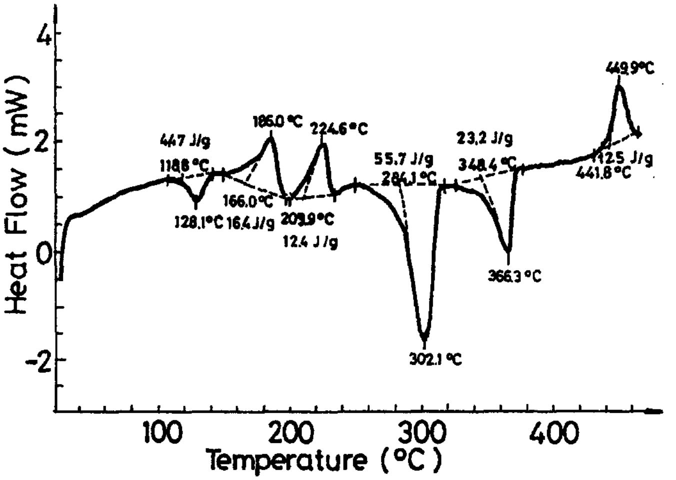


Fig. 5 DSC curve of MoO_2L obtained by isothermal heating of $[MoO_2(L)S]$; in hydrogen at a heating rate of 20°C min^{-1}

(300–500°C) show two exothermal peaks which, in this case, point to the oxidative nature of the decomposition of the tridentate ligand. The degradation of all the investigated complexes finally yield MoO_3, which was confirmed by IR spectra.

All the presented data point to complex processes of structural transformations and thermal decomposition, which can be summarized as follows:

$$[MoO_2(L)S] \xrightarrow{-S} MoO_2L \xrightarrow{\approx 120^{\circ}C} (MoO_2L)_n \xrightarrow{-L} MoO_3$$

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