Dioxomolybdenum(VI) Complexes with 2α-Hydroxybenzimidazoles and Their ^{95}Mo NMR Spectra

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Abstract

Complexes of a series of 2α-hydroxybenzimidazoles (L) with Mo(VI) are reported. In most cases the complexes form readily on reaction of $MoO_2(AcAc)_2$ with L in acetone or ethanol. Electronic spectra, infra red spectra, magnetic measurements, ^{1}H and ^{95}Mo NMR results are reported for the complexes which have MoO_2L_2 or $MoO_2L_2(Solvent)_1$, stoichiometry. The physical measurements are best interpreted in terms of distorted octahedral *cis*-dioxoMo(VI) complexes with a 4O, 2N donor set. This is confirmed for the complex with 2α-hydroxybenzylbenzimidazole (HBB) by an X-ray crystallographic study which also shows that HBB coordinates through its imino nitrogen and alkoxy oxygen atoms.

Introduction

2α-hydroxybenzimidazoles (Fig. 1) form a variety of complexes with first row transition metal ions [1].

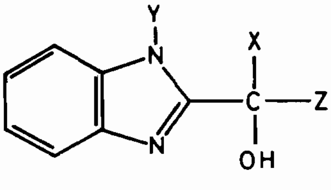

Fig. 1. 2α-hydroxybenzimidazole.

One of these complexes *viz.* $Ni(L)_2(L')_1(ClO_4)_1$ where L is Fig. 1 with Y = $CH_2CH_2CH_3$, X = H and Z = C_6H_5 and L′ the deprotonated form has been shown from an EXAFS study to be a good model for the active site of the enzyme urease [2].

Since molybdenum is a metal of considerable biological importance we have investigated the complexes formed between Mo(VI) and ligands of the type shown in Fig. 1. The following abbreviations are used throughout this paper. Fig. 1 with: X = H, Z = H, Y = H is 2α-hydroxymethylbenzimidazole ≡ HMB; X = H, Z = CH_3, Y = H is 2α-hydroxyethylbenzimidazole ≡ HEB; X = CH_3, Z = CH_3, Y = H is 2α-hydroxyisopropylbenzimidazole ≡ HIB; X = H, Z = C_6H_5, Y = H is 2α-hydroxybenzylbenzimidazole ≡ HBB; X = H, Z = C_6H_5, Y = $CH_2CH_2CH_3$ is 1N-n-propyl-2α-hydroxybenzylbenzimidazole ≡ NPHBB; X = H, Z = C_6H_5, Y = CH_3CHCH_3 is 1N-iso-propyl-2α-hydroxybenzylbenzimidazole ≡ IPHBB; X = H, Z = C_6H_5, Y = $CH_2CH_2OCH_3$ is 1N-(2′methoxyethyl)-2α-hydroxybenzylbenzimidazole ≡ MEHBB.

Experimental

Syntheses

2α-hydroxybenzimidazoles were synthesized by condensation of the appropriate substituted orthophenylene diamine and hydroxycarboxylic acid [3]. The complexes were prepared using the following general method. Ethanolic (or acetone) solutions of $MoO_2(AcAc)_2$ (0.005 mol) and ligand (0.010 mol) were mixed with rapid stiring and the product filtered off after about one hour. The product was washed with ethanol and dried at 50 °C under vacuo. This method gave no product for L = HBB and so the following procedure was used. An ethanolic solution of MoO_2Cl_2 (0.010 mol) and tetrahydrofuran solution of the sodium salt of HBB were stirred together for ninety minutes under an atmosphere of dry dinitrogen. The white product was filtered and recrystallised from ethanol to give very pale lilac prisms one of which was used for the X-Ray study. Analytical results are given in Table I.

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X-Ray Study

Full experimental details of this are given elsewhere [4].

^{95}Mo Nuclear Magnetic Resonance Study

Spectra were obtained on naturally abundant samples with a Bruker WM-250 spectrometer operating at 16.30 MHz. All samples were run at room temperature in 10 mm tubes containing a coaxial 5 mm tube filled with deuterium oxide (the deuterium resonance was used for field lock). The spectra were run using a 50 KHz sweep width and a 40 msec acquisition time. The radio frequency pulse width was adjusted to give a 30° tip angle. All free induction decays (FID's) were multiplied by an exponential window function adjusted to give a minimum observable line width of twice the digital resolution (actual line widths in all spectra were much greater). Chemical shifts expressed as δ values in ppm were measured relative to an external standard of 1 M aqueous Na_2MoO_4. The accuracy of shift measurements decreases with increasing line width, for the widest lines observed it is approximately 5 ppm. All solutions of the complexes in dimethylformamide DMF and dichloromethane DMC were saturated. Acoustic ringing in the nmr probe coils can create significant problems in these low frequency wide sweep experiments, the spurious signal from the probe masks the early part of the FID.

Reflectance spectra were obtained with a Beckman DK 2A spectrometer, solution spectra with a Pye Unicam SP8-150 UV/visible spectrophotometer.

Magnetic moments were measured at room temperature on a conventional Gouy balance.

Results

Most of the ligands react readily with MoO$_2$(AcAc)$_2$ to form complexes of stoichiometry MoO$_2$L$_2$(Solvent)$_n$ (where $n = 0$ or 1). Surprisingly HBB boiled under reflux with MoO$_2$(AcAc)$_2$ for many hours produced only a very low yield of impure product. To form MoO$_2$(HBB)$_2$(Solvent)$_1$ it was necessary to react the sodium salt of HBB with MoO_2Cl_2. This lack of reactivity towards MoO$_2$(AcAc)$_2$ could be due to stronger intermolecular hydrogen bonding in HBB than is found in the other ligands. This is suggested by the melting point of HBB which is at least 30 °C higher than that of any of the other ligands. The absence of the ligand O–H stretching frequency in the infrared spectra of the complexes indicates that the ligand hydroxyl proton is lost on coordination to molybdenum, Table II. The bands in the region 520–650 cm^{-1} are assigned to the ligand oxygen molybdenum stretch [5, 6], and the two very strong bands at 900 (±25) cm^{-1} are typical for Mo(VI) multiply bonded to two terminal oxygen atoms in a *cis* configuration [7, 8].

The infrared vibrations associated with the solvent molecules in MoO$_2$L$_2$(Solvent)$_1$ together with the lowering of the N–H stretching frequency, indicate that the ethanol, acetone and dimethylformamide are hydrogen bonded in these complexes.

The proton nmr spectra of the solvates, Table III, are all sharp as would be expected for diamagnetic Mo(VI) complexes. The UV/visible spectral data are collected in Table IV. All the compounds in the finely divided state are white except MoO$_2$(IPHBB)$_2$ which is very pale blue. In solution the absorption bands of all the complexes are similar and assigned to ligand to metal charge transfer transitions [9]. All the solutions obeyed Beer's Law. The solid state diffuse reflectance spectrum of the pale blue MoO$_2$(IPHBB)$_2$ exhibits a weak absorption at 14,950 cm^{-1} (this is not seen in solution). Except for MoO$_2$(IPHBB)$_2$ and MoO$_2$(HIB)$_2$ the complexes are diamagnetic, Table IV. MoO$_2$(IPHBB)$_2$ is slightly paramagnetic and this is probably related to the weak absorption at 14,950 cm^{-1} seen in the diffuse reflectance spectrum. The ^{95}Mo nmr data for the

TABLE I. Analytical Results for the Complexes.

Complex	Found				Calculated			
	Mo	C	H	N	Mo	C	H	N
MoO$_2$(HMB)$_2$	22.8	45.8	3.6	13.5	22.7	45.5	3.3	13.3
[MoO$_2$(HEB)$_2$](C$_2$H$_5$OH)$_1$	19.4	48.1	5.0	11.2	19.3	48.4	4.9	11.3
[(MoO$_2$(HEB)$_2$](DMF)$_1$[a]	18.1	48.4	4.9	13.3	18.3	48.2	4.8	13.4
MoO$_2$(HIB)$_2$	19.8	49.2	4.8	11.6	20.0	50.2	4.6	11.7
[MoO$_2$(HBB)$_2$](C$_2$H$_5$OH)$_1$	15.6	57.9	4.5	9.0	15.5	58.1	4.6	9.0
[MoO$_2$(HBB)$_2$](Acetone)$_1$[b]	15.0	58.8	4.4	8.9	15.2	58.9	4.5	8.9
MoO$_2$(NPHBB)$_2$	14.9	61.7	5.1	8.4	14.6	62.0	5.2	8.5
MoO$_2$(IPHBB)$_2$	14.8	61.9	5.4	8.7	14.6	62.0	5.2	8.5
MoO$_2$(MEHBB)$_2$	14.1	59.2	5.4	8.4	13.9	59.1	5.0	8.1

[a] DMF = dimethylformamide. This complex was prepared by recrystallising [MoO$_2$(HEB)$_2$](C$_2$H$_5$OH)$_1$ from dimethylformamide.
[b] This complex was prepared by recrystallising [MoO$_2$(HBB)$_2$](C$_2$H$_5$OH)$_1$ from acetone.

TABLE II. Infrared Spectral Data.

	ν(O–H)	ν(N–H)	ν(Mo=Ot)	ν(Mo–O)	Others
HMB	2664m,br	3260,br			
MoO$_2$(HMB)$_2$		3300m,br	916vs 880vs	622m 576m 539s,br	
HEB	2700s,br	3130s,br			
[MoO$_2$(HEB)$_2$](EtOH)$_1$	3360m,br	3110s,br 3050s,br	900vs 875vs	586s,br 520m	ν(C–O) 1065m
[(MoO$_2$(HEB)$_2$](DMF)$_1$		3110s,br 3060s,br	902s 875vs	587s 563s	ν(C=O) 1644br δ(NCO) 662m
HIB	2700m,br	3140m,br			
MoO$_2$(HIB)$_2$		3180s	915vs,890vs	660m,590m,br	
HBB	2650m,br	3240m,br			
[MoO$_2$(HBB)$_2$](EtOH)$_1$	3320m,br	3110m,br	917s 885vs,br	631m 577m,br	ν(C–O) 1087m
[MoO$_2$(HBB)$_2$](Acetone)$_1$		3110m	928s,br 898vs	633m 578m	ν(C=O) 1699m,br
NPHBB	3140m,br				
MoO$_2$(NPHBB)$_2$			915s 900vs	641m 624w 591m	
IPHBB	3130m,br				
MoO$_2$(IPHBB)$_2$			917s 899vs	635s 584m	
MEHBB	3170m,br				ν(C–O–C) 1129vs
MoO$_2$(MEHBB)$_2$			910vs 898vs	632m 598s	ν(C–O–C) 1129m

TABLE III. ^{1}H NMR Data.

Compound	Position	Multiplicity	Ratio	Assignment
MoO$_2$(HMB)$_2$ [a]	12.86	s (broad)	1	N–H of HMB
	7.40–7.76	m	4	Phenyl protons
	5.70	s	2	CH$_2$ protons of HMB
[MoO$_2$(HEB)$_2$](EtOH)$_1$ [a]	12.98	s (broad)	2	2 × N–H of HEB
	7.48–7.88	m	8	2 × phenyl protons
	5.88	q (J = 6.8 Hz)	2	2 × CH proton of HEB
	4.4	s (broad)	1	O–H of ethanol
	3.48	q (J = 6.8 Hz)	2	CH$_2$ protons of ethanol
	1.66	d (J = 6.9 Hz)	6	2 × CH$_3$ protons of HEB
	1.17	t (J = 6.9 Hz)	3	CH$_3$ protons of ethanol
[(MoO$_2$(HEB)$_2$](DMF)$_1$ [a]	12.97	s (broad)	2	2 × N–H of HEB
	7.96	s	1	CH proton of DMF
	7.18–7.83	m	8	2 × phenyl protons
	5.88	q (J = 6.6 Hz)	2	2 × CH proton of HEB
	2.83	s	3	(CH$_3$)$_2$ protons of DMF
	2.76	s	3	(CH$_3$)$_2$ protons of DMF
	1.67	d (J = 6.5 Hz)	6	2 × CH$_3$ protons of HEB

(continued overleaf)

TABLE III *(continued)*

Compound	Postion	Multiplicity	Ratio	Assignment
$MoO_2(HIB)_2$ [a]	13.1	s	2	2 × N–H of HIB
	7.03	m	8	2 × phenyl protons of HIB
	1.76	m	12	2 × CH_3 of HIB
$[MoO_2(HBB)_2](EtOH)_1$ [a]	12.89	s	2	2 × N–H of HBB
	7.26–8.02	m	18	2 × phenyl protons of HBB
	6.71	s	2	2 × CH proton of HBB
	4.16	s (broad)	1	O–H of ethanol
	3.32	q (J = 6.8 Hz)	2	CH_2 protons of ethanol
	1.06	t (J = 6.9 Hz)	3	CH_3 protons of ethanol
$[MoO_2(HBB)_2](Acetone)_1$ [a]	12.90	s (broad)	2	2 × N–H of HBB
	7.26–8.03	m	18	2 × phenyl protons of HBB
	6.72	s	2	2 × CH protons of HBB
	2.08	s	6	$(CH_3)_2$ protons of acetone
$MoO_2(NPHBB)_2$ [b]	7.15–8.20	m	9	Phenyl protons
	6.60	s	1	CH proton of NPHBB
	3.05–3.77	m	2	CH_2 protons of n-propyl group
	0.63–1.05	m	2	CH_2 protons of n-propyl group
	0.14	t (J = 7.0 Hz)	3	CH_3 protons of n-propyl group
$MoO_2(IPHBB)_2$ [b]	7.20–8.20	m	9	Phenyl protons
	6.60	s	1	CH protons of NPHBB
	4.23	septet (J = 6.4 Hz)	1	CH proton of iso-propyl group
	0.98	d (J = 7.4 Hz)	3	CH_3 protons of iso-propyl group
$MoO_2(MEHBB)_2$ [b]	7.27–8.23	m	9	Phenyl protons
	6.74	s	1	C–H proton
	3.85	m	2	CH_2 protons of $CH_2CH_2OCH_3$
	3.10	m	2	CH_2 protons of $CH_2CH_2OCH_3$
	2.85	s	3	CH_3 protons of the methoxy group

[a] in d_6-Dimethylsulphoxide (DMSO). [b] in d_2-Dichloromethane (DCM).

complexes are listed in Table V. The chemical shifts for all the complexes fall within the range expected for six coordinate cis dioxomolybdenum(VI) complexes with N and O donor ligands [10, 11].

The structure of $MoO_2(HBB)_2(Ethanol)_1$ as revealed by X-ray crystallography is shown in Fig. 2. The physical measurements of this complex are in accord with its structure and since the physical measurements of the other complexes are similar to those of $MoO_2(HBB)_2(Ethanol)_1$, it is reasonable to assume that they have the same type of structure.

Given that the accuracy of the ^{95}Mo chemical shift measurements for the widest lines observed is only ±5 ppm it is still possible to divide the complexes into two groups to facilitate a discussion of these shifts based on the structural type in Fig. 2.

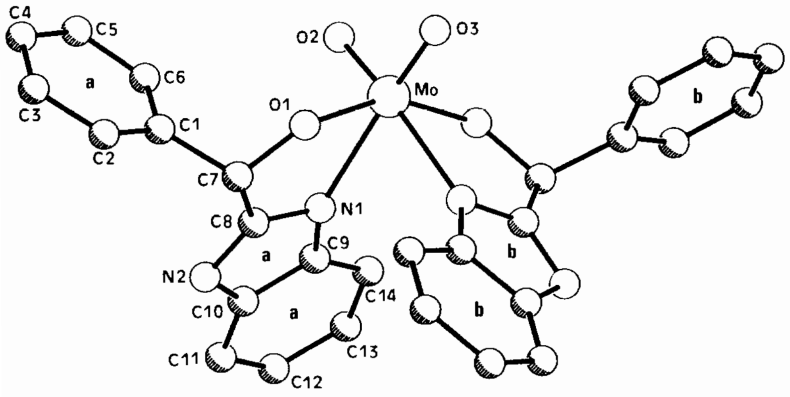

Fig. 2. Structure of $MoO_2(HBB)_2(Ethanol)_1$.

TABLE IV. UV/Visible Spectral Data and Room Temperature Magnetic Data.

1) Solution Spectra[a]	Band Maxima (cm^{-1})				
$MoO_2(HMB)_2$		37,000sh	36,350	35,600	
$[MoO_2(HEB)_2](EtOH)_1$		37,300sh	36,500	35,600	
$[MoO_2(HEB)_2](DMF)_1$		37,300sh	36,500	35,600	
$MoO_2(HIB)_2$		40,000sh	36,630	35,970	
$[MoO_2(HBB)_2](EtOH)_1$		37,450sh	36,350	35,500	
$[MoO_2(HBB)_2](Acetone)_1$		37,450sh	36,350	35,500	
$MoO_2(NPHBB\}_2$		37,200	36,250	35,350	
$MoO_2(IPHBB)_2$		37,000	36,250	35,350	
$MoO_2(MEHBB)_2$		37,300	36,350	35,350	
2) Solid State Spectra[b]					
$MoO_2(NPHBB)_2$		8,750	7,150	5,950	5,350
$MoO_2(IPHBB)_2$	14,950	8,750	7,200	5,950	5,380
	Molar Susceptibility × 10^{-6} (cgsu)		Diamagnetic Correction × 10^{-6} (cgsu)		
$Mo_2(HMB)_2$	−162		151		
$[MoO_2(HEB)_2](EtOH)_1$	−218		209		
$[MoO_2(HEB)_2](DMF)_1$	−222		217		
$MoO_2(HIB)_2$	−140		211		
$[MoO_2(HBB)_2](EtOH)_1$	−284		281		
$[MoO_2(HBB)_2](Acetone)_1$	−345		289		
$MoO_2(NPHBB)_2$	−292		315		
$MoO_2(IPHBB)_2$	−171		315		
$MoO_2(MEHBB)_2$	−316		324		

[a] In DMF, 1 cm silica cells. All values of $\epsilon > 10{,}000$ $dm^3\,mol^{-1}\,cm^{-1}$. [b] Diffuse reflectance.

TABLE V. ^{95}Mo NMR Spectral Data of the Complexes.[a]

	Solvent	δ(ppm)	$\Delta\nu_{1/2}$(Hz)
$MoO_2(HMB)_2$	DMF	57.4	260
$[MoO_2(HEB)_2](EtOH)_1$	DMF	39.6	490
$[MoO_2(HBB)_2](EtOH)_1$	DMF	56.3	374
$MoO_2(HIB)_2$	DMF	37.4	360
$[MoO_2(HBB)_2](Acetone)_1$	DMF	54.5	382
$MoO_2(NPHBB)_2$	DCM	50.0	170
$MoO_2(IPHBB)_2$	DCM	48.6	245
$MoO_2(IPHBB)_2$	DMF	48.7	410
$MoO_2(MEHBB)_2$	DCM	50.4	195

[a] All solutions were saturated. DMF: Dimethylformamide. DCM: Dichloromethane. δ: Chemical Shift. $\Delta\nu_{1/2}$: Line width at half peak height.

$MoO_2(HMB)_2$ gives a shift of 57.4 ppm and on substitution of the α carbon protons by methyl groups to give $MoO_2(HEB)_2$ and $MoO_2(HIB)_2$ this is observed to fall to 39.6 ppm ($MoO_2(HEB)_2$) and 37.4 ppm ($MoO_2(HIB)_2$). A possible explanation for this is that the methyl group(s) being electron releasing increase the electron density on the donor oxygen atom and hence increase the shielding of the ^{95}Mo nucleus. A similar explanation could apply to the decrease in shifts observed in going from $MoO_2(HBB)_2$ at 55.6 ppm to between 50.4 and 48.6 ppm for $MoO_2(MEHBB)_2$, $MoO_2(IPHBB)_2$ and $MoO_2(NPHBB)_2$ *i.e.* the electron releasing substituents on the amino nitrogen increase the electron density on the donor nitrogen thus increasing the shielding on the ^{95}Mo NMR nucleus.

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