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Synthesis, Characterisation and Biological Activity of Oxovanadium(IV), Thorium(IV) and Dioxouranium(VI) Complexes of N-(1-piperidinobenzyl)urea and N,N′-bis(N-morpholinobenzyl)urea

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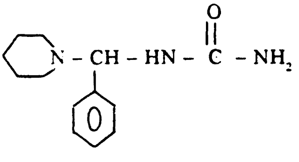
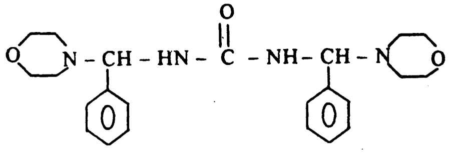
The new complexes of oxovanadium(IV), thorium(IV) and dioxouranium(VI) with N-(1-piperidinobenzyl) urea (PBU) and N,N′-bis(N-morpholinobenzyl) urea (MBU) have been synthesised and characterised by elemental analysis, molar conductance, magnetic susceptibility, electronic, IR, ^{1}H NMR and thermal studies. From the IR and PMR spectral data, the ligands are suggested to behave as O, N donors. PBU coordinates through N atom of piperidine ring and O atom of urea fragment while MBU acts as a tridentate ligand coordinating through N atoms of two morpholine rings and O atom of urea moiety. The complexes have also been screened *in vitro* for antibacterial activities.

INTRODUCTION

Urea and related compounds have been investigated in detail for their donor properties and biological activities[1]. Studies of metal complexes of aminomethy-



(PBU)



(MBU)

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lated Mannich base N-morpholinomethylurea produced by using urea, morpholine and formaldehyde have been reported in literature[2]. Recently we have reported the complexing effect of various transition metal ions with amino benzylated Mannich bases N-(1-piperidinobenzyl) urea (PBU) and N,N′-bis(N-morpholinobenzyl) urea (MBU) prepared by condensation of urea, piperidine/-morpholine and benzaldehyde[3]. In continuation of our work, we present here the isolation, characterisation and antimicrobial activity of oxovanadium(IV) sulphate, thorium(IV) nitrate and dioxouranium(VI) nitrate complexes of PBU (1a–1c) and MBU (2a–2c).

EXPERIMENTAL

Chemicals used were either of BDH or E. Merck quality. Metal salts and solvents were of reagent grade. The ligands PBU and MBU were prepared by following the reported methods[3]. The purity of the samples was checked by m.p., TLC and C, H and N analyses. The ligands being insoluble in water, all the complexes were prepared in non-aqueous media. The metal salts were used as such without dehydrating them, since dehydrated salts are insoluble in alcohol.

Preparation of metal complexes of PBU (1a–1c)

General procedure: The metal complexes were prepared by mixing the solutions of the ligand in chloroform and metal salt in *n*-butanol/methanol in 2 : 1 mole ratio. The resultant colloidal solution was digested on the water bath about 15 min. The solid complex was washed successively with methanol, acetone and finally dried *in vacuo.*

Preparation of metal complexes of MBU (2a–2c)

General Procedure: A mixture of the solutions of the ligand in chloroform and metal salt in dry ethanol in equimolar ratio was refluxed on the water bath for 1 h. The resultant semi-solid complex was kept at 10°C in ice bath and stirred. The solid was washed with acetone and dried over anhydrous $CaCl_2$.

Metal ions and anions in the complexes were determined by standard methods[4]. C, H and N contents of the complexes were analysed by Carlo Erbo 1106, Thomas C, H and Coleman N microanalysers. The analytical data of the complexes are presented in Table-1.

IR spectra in KBr pellets on a Perkin-Elmer 597, PMR spectra ($CDCl_3$/DMSO–d_6) on Jeol GS × 400 and electronic spectra in DMF on a Cecil CE 5501 spectrophotometer were recorded. Room temperature magnetic susceptibilities were measured by Gouy's method and thermal analyses were carried out by Netsch 429. The antibacterial activities of the ligands and metal complexes were assayed in biochemistry branch of our department. Simultaneous recordings of TGA and DTA were carried out at a heating rate of 10° min^{-1} in air using 50–100 mg of the sample in each case.

RESULTS AND DISCUSSION

All the complexes (**1a–2c**) are stable in air and non-hygrogscopic They are soluble in DMF and DMSO. The analytical results (Table-1) indicate a 1 : 1

(M : L) stoichiometry for all the complexes. Except the complex (**2a**), the other complexes in DMF at 10^{-3} M show low molar conductivity values in the range of 15.58–37.28 Λ^{-1} cm^2 mol^{-1} (Table-1) indicating their non-electrolytic nature. The complex (**2a**) exhibits the molar conductance 92.08 Λ^{-1} cm^2 mol^{-1} suggesting the 1 : 1 electrolytic behaviour.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE COMPLEXES (**1a–1c** and **2a–2c**)

S. No.	Complex (% yield), Dec. Temp. °C, Colour	% Found (Calc.)				Λ_M Λ^{-1}cm^2 mol^{-1}	λ_{max} (cm^{-1})
		M	C	N	H		
1a	(VO. PBU. SO_4)						
	(57), 176	20.01	39.20	10.73	4.01	15.58	15,000
	Pale Green	(20.51)	(39.39)	(10.61)	(4.09)		
1b	(Th. PBU. $(NO_3)_4$)	31.53	21.46	13.51	2.48		
	(52), 218	(32.02)	(21.88)	(13.74)	(2.66)	14.60	—
	White						
1c	(UO_2. PBU. $(NO_3)_2$)	29.83	24.76	11.02	3.16		
	(61), 215	(40.0)	(24.88)	(11.16)	(3.0)	11.59	20,060
	Yellow						
2a	(VO. MBU) SO_4	18.31	48.03	19.77	5.24	92.08	13,060
	(56), 190	(18.0)	(48.17)	(19.69)	(4.32)		17,100
	Pale Green						
2b	(Th. MBU. $(NO_3)_4$)	26.01	30.72	12.59	3.87		
	(50), 210	(26.13)	(31.0)	(12.79)	(4.20)	37.28	—
	White						
2c	(UO_2. MBU. $(NO_3)_2$)	29.69	34.01	10.45	3.83		
	Yellow	(30.03)	(34.33)	(10.76)	(4.09)	16.85	19,950

Infrared spectra: The ligand PBU and its complexes (**1a–1c**) exhibit two smooth bands at 3460 (asymmetric ν(NH)) and 3360 cm^{-1} (symmetric ν(NH)).[3] The persistence of these bands in the complexes indicates non-involvement of the nitrogens of urea moiety in coordination. The ligand bands at 1630 (νC=O) and 1100 cm^{-1} (piperidine ν(CNC)) undergo a downward shift in the complexes suggesting the bidentate nature of PBU bonding through carbonyl oxygen and piperidine nitrogen.

The ligand MBU exhibits four intense bands at 3330 (νNH), 1635 ν(C=O), 1130 (piperidine ν(CNC)) and 1100 cm^{-1} (morpholine ν(COC))[3]. In the spectra of the complexes (**2a–2c**) the ν(C=O) and ν(CNC) bands display substantial negative shifts with considerable low intensity indicating the coordination of MBU through oxygen of amide moiety and nitrogens of the two morpholine entities. There is no change in the positions of bands due to ν(NH) and ν(COC) modes which suggests that nitrogens of amide and oxygen of morpholine rings are not involved in coordination. A strong ν(V=O) band[6] in the spectra of complexes **1a** and **2a** appears around 980 cm.$^{-1}$ The complexes of UO_2^{VI} display very strong bands at 930–910 cm^{-1} assignable to ν(O=U=O) modes.[7]

Thorium(IV) nitrato complexes (1b and 2b) and dioxouranium(VI) nitrato complexes (**1c** and **2c**) exhibit additional bands in the ranges 1415–1380 (ν_5) and 1360–1340 cm^{-1} (ν_1) assignable to ν(N—O) modes of the co-ordinated nitrate groups. Since the ν_5 and ν_1 bands are separated to an extent of 50–70 cm^{-1}, it shows the unidentate behaviour of the nitrato groups in these complexes. The observed bands at 1120 and 1050 (ν_3), 1000 (ν_1) and 620 cm^{-1} (ν_4) in the spectrum of the complex (**1a**) suggest the unidentate nature of the sulphato group. The free sulphate ion of the complex (**2a**) exhibits two bands at 1106 (ν_3) and 615 cm^{-1} (ν_4). The appearance of two bands in the region 470–430 cm^{-1} in the spectra of all the complexes (**1a–2c**) is assignable to ν(M—N) and ν(M—O) modes[8].

PMR Spectra: The spectrum of ligand PBU exhibits multiplets at δ 7.6–7.31 (ArH), 5.45–5.68 (amide NH) and 2.4 ppm (piperidine N—CH_2).[9] In the spectra of its complexes (**1a–1c**), the signal of amide NH protons has shifted slightly downfield (δ 6.10–5.75) indicating the coordination of carbonyl oxygen of PBU. The slight shift is due to less shielding of NH protons since the electron pair on nitrogen undergoes a drift towards carbonyl group upon oxygen coordination. The signal due to piperidine N—CH_2 protons is also found slightly shifted downfield denoting coordination of piperidine nitrogen atom[9]. Thus PMR and IR results confirm the bidentate nature of PBU ligand.

The ligand MBU shows broad signals at δ 7.37 (ArH), 5.40 (amide NH), 3.70 (morpholine N—CH_2) and 2.52 (morpholine O—CH_2).[3] The spectra of the complexes of MBU (**2a–2c**) display slight downfield shifts in the signals due to amide NH protons and morpholine N—CH_2 protons suggesting tridentate behaviour of the ligand bonding through tertiary nitrogens of both morpholine rings and carbonyl oxygen.

Magnetic susceptibility and electronic spectra: The room temperature magnetic moments of the VO(IV) complexes (**1a** and **2a**) are 1.78 and 1.82 BM. The electronic spectrum of the complex (**1a**) exhibits a broad band at 15000 cm^{-1} assignable to $^2E \longrightarrow {}^2B_1$ transition. The complex (**2a**) shows two bands at 13060 and 17000 cm^{-1} corresponding to $^2E \longrightarrow {}^2B_1$ and $^2B_2 \longrightarrow {}^2B_1$ transitions which are in agreement with four coordinated structures of the complexes (**1a** and **2a**)[10].

The low magnetic moment values of Th(IV) and UO_2(VI) complexes fall in the range of 0.10–0.32 BM which suggest diamagnetic character of the complexes. The weak absorption band around 20,000 cm^{-1} observed in the spectra of UO_2(VI) complexes may be due to electronic transition within the ligand itself[11].

Thermal analysis: The VO(IV) complexes (**1a**) and (**2a**) are found stable up to 176 and 190°C crespectively. The TG curve of (**2a**) shows the steady weight loss in the range of 200–360°C. The strong exotherm at 245°C and weak exotherm at 280°C in DTA of the complex (1a) indicate the oxidation of PBA moiety. The TG curve of the complex (**2b**) shows no loss of weight up to 210°C. The endothermic peaks at 265°C and 305°C in DTA thermogram of this complex reveal decomposition at these temperatures. TG and DTA patterns of the complex (**1c**) reveal decomposition at 215°C and oxidation at 285°C. The final residues of the complexes at 600°C are found to be their metal oxides. Thermal stabilities of the metal complexes are in the order of Th > U > V.

Antimicrobial screening: The ligands PBU, MBU and their complexes were tested for antibacterial activity by serial tube dilution technique[12] at different concentrations against *E. coli* (gram-negative) and *S. aureus* (gram-positive) microbes. A nutrient neutral broth medium of 3% (v/v) Soyabeen Casein and inocula from 1 or 2 days old cultures grown on yeast-nitrogen base were prepared and the assay tubes were incubated at 37°C for two days. The percentage of inhibition of growth was calculated as follows:

$$\% \text{ inhibition} = 100\,(P-Q)/P$$

where P = turbidity without the test sample and Q = turbidity with the test sample.

The results (Table-2) reveal that the activity of the compounds increases with increase in concentration. The metal complexes show more activity than free ligands. MBU and its complexes seem to exhibit lower activity than PBU and its complexes.

TABLE-2
PERCENTAGE INHIBITION OF BACTERIAL GROWTH

Compounds	*S. aureus* Concentrations (μg/mL)			*E. coli* Concentrations (μg/mL)		
	300	200	100	300	200	100
PBU	63.7	51.1	35.7	78.0	62.2	46.1
($VO\cdot PBU\cdot SO_4$)	78.4	58.2	42.2	89.3	68.2	49.7
($Th.PBU\cdot(NO_3)_4$)	68.6	54.1	35.9	81.5	65.2	45.2
($UO_2\cdot PBU\cdot(NO_3)_2$)	66.5	52.3	38.1	82.3	70.4	51.0
MBU	46.7	40.2	23.0	64.1	46.5	32.6
($VO\cdot MBU)\cdot SO_4$	53.3	46.8	28.1	68.4	53.1	36.2
($Th.MBU\cdot(NO_3)_4$)	50.0	40.9	23.3	64.6	46.6	33.0
($UO_2\cdot MBU\cdot(NO_3)_2$)	52.75	42.4	24.6	54.4	37.8	28.7

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