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Synthesis and characterization of peroxo complexes of uranium(VI) with some Mannich base ligands

Balgar Singh · Simpy Mahajan · Haq N. Sheikh · Mohita Sharma · Bansi L. Kalsotra

Abstract Uranium(VI) peroxo complexes of composition $[UO(O_2)L–L(NO_3)_2]$, where L–L are the Mannich base ligands morpholinobenzyl urea, piperidinobenzyl urea, morpholinobenzyl thiourea, piperidinobenzyl thiourea, morpholinomethyl thiourea, piperidinomethyl thiourea, or morpholinomethyl urea, are reported. The synthesized complexes were characterized by use of a variety of physicochemical techniques, viz. elemental analysis, molar conductivity, magnetic susceptibility measurements, IR, electronic, mass, ^1H NMR, and ^{13}C NMR spectroscopy, and TGA/DTA studies. These studies revealed that the complexes are both non-electrolytic and diamagnetic in nature. The ligands are bound to the metal in a bidentate mode through carbonyl oxygen or thiocarbonyl sulfur and the ring nitrogen. Mass spectra confirm the molecular mass of the complexes. The antifungal activity of the complexes is greater than that of the corresponding free ligands.

Keywords Antifungal activity · Coordination chemistry · Mannich bases · ^{13}C NMR · Peroxo complexes

Introduction

Studies on peroxo complexes have received substantial encouragement in recent years, because of their application as oxidants in synthetic organic chemistry [1–12]. Many peroxo complexes are a source of active oxygen atoms and can be used as catalysts of oxygen-insertion reactions with organic and inorganic substrates [13–17], and are of biochemical relevance [18–25]. They are widely used, for example, in the oxidation of thioanisole [26, 27], methylbenzenes [28], tertiary amines, alkenes, alcohols [29, 30], and bromide [31], and also in olefin epoxidation [32–36]. Peroxo complexes of molybdenum and tungsten are attracting interest as oxidants in organic synthesis [37]. Because uranium somewhat resembles the group 6B elements, it was of interest to discover whether it would form analogous peroxo complexes which contain organic moieties. The ubiquity of the UO_2 group distinguishes uranium from molybdenum and tungsten, however, and this factor may have hitherto prevented the generation of peroxo complexes from uranyl salts and organic reagents. A variety of peroxo complexes of uranium with organic ligands have been reported [38]. The coordination numbers for metal chelates of Th(IV) and UO_2(VI) have been reported [39, 40].

Metal complexes of Mannich bases have been of vital importance in the development of coordination chemistry [41, 42]. There has been much interest in the synthesis and characterization of transition metal complexes containing a Mannich base, because of their varied pharmaceutical properties [43–47]. Synthesis of N-(morpholinobenzyl)urea and thiourea and their complexation with molybdenum and tungsten has been reported [22, 23, 25]. In this manuscript we describe the synthesis and characterization of peroxo complexes of uranium(VI) with some formaldehyde and benzaldehyde-based Mannich base ligands. The structures of ligands are given in Scheme 1.

Results and discussion

The analytical and physical data of the complexes are listed in Table 1. The analytical data are in good agreement with

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the general molecular formula proposed for the complexes, [UO(O$_2$)L–L(NO$_3$)$_2$] (where L–L is morpholinobenzyl urea (MBU), piperidinobenzyl urea (PBU), morpholinobenzyl
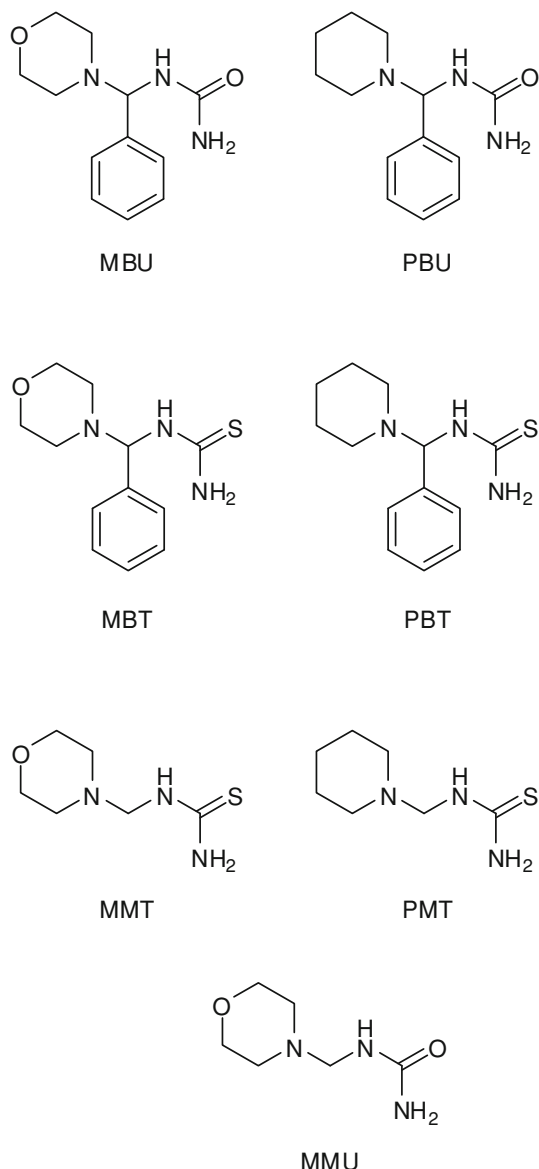
thiourea (MBT), piperidinobenzyl thiourea (PBT), morpholinomethyl thiourea (MMT), piperidinomethyl thiourea (PMT), or morpholinomethyl urea (MMU)). The isolated solid complexes are stable to air and light and are insoluble in common organic solvents but soluble in DMSO and DMF. All the complexes are yellowish coloured. All complexes decompose on heating and do not have sharp melting points.

Conductance and magnetic measurements

The molar conductivity Λ of the complexes measured in DMF solution lies in the range 14–19 S cm^2 mol^{-1}, which indicates the non-electrolytic nature of these complexes (Table 1) [48]. Moreover, magnetic studies show that all the complexes are diamagnetic as expected for the d^0 system of uranyl(VI) peroxo complexes.

IR spectral studies

The characteristic IR absorption of the ligands and complexes, and their assignments, are given in Table 2. The IR spectra of all the complexes contain bands characteristic of coordinated oxo and peroxo groups and the ligand molecule. The metal peroxo group gives rise to three IR active vibrational modes of v(O–O), v_{asym}(UO$_2$), and v_{sym}(UO$_2$). These characteristic vibration modes appear around 875–905, 712–750, and 630–674 cm^{-1}, respectively. These bands confirm the η^2-coordination of the peroxo group [49]. In all the complexes, an additional sharp band around 995–1,002 cm^{-1} has been assigned to the v(U=O) mode [18, 38]. Thus, IR the spectra confirm the presence of the [UO(O$_2$)]$^{2-}$ moiety in these complexes.

To study the mode of binding of the Mannich base ligands with uranium in the peroxo complexes, the IR spectra of the free ligands were compared with those of corresponding metal complexes (Table 2). In the spectra of the ligands MBU, PBU, and MMU a sharp band assigned to v(C=O) of the amide group and another band assigned to v(C–N–C) of the morpholine/piperidine ring undergo negative shift in the respective complexes. Also, bands assigned to

Scheme 1

Table 1 Analytical data and some physical properties of uranium(VI) peroxo complexes

Complex	Empirical formula (MW/g mol^{-1})	Colour	Dec. temp/°C	Λ/S cm^2 mol^{-1}
[UO(O$_2$)MBU(NO$_3$)$_2$]	C$_{12}$H$_{17}$N$_5$O$_{11}$U (645.32)	Lt. yellow	>300	18
[UO(O$_2$)PBU(NO$_3$)$_2$]	C$_{13}$H$_{19}$N$_5$O$_{10}$U (643.33)	Yellow	>280	15
[UO(O$_2$)MBT(NO$_3$)$_2$]	C$_{12}$H$_{17}$N$_5$O$_{11}$SU (661.37)	Yellow	>290	19
[UO(O$_2$)PBT(NO$_3$)$_2$]	C$_{13}$H$_{19}$N$_5$O$_9$SU (659.39)	Lt. yellow	>300	14
[UO(O$_2$)MMT(NO$_3$)$_2$]	C$_6$H$_{13}$N$_5$O$_{10}$SU (585.27)	Lt. yellow	>295	16
[UO(O$_2$)PMT(NO$_3$)$_2$]	C$_7$H$_{15}$N$_5$O$_9$SU (583.30)	Yellow	>310	19
[UO(O$_2$)MMU(NO$_3$)$_2$]	C$_6$H$_{13}$N$_5$O$_{11}$U (569.21)	Yellow	>313	17

Table 2 Selected FT-IR data (cm^{-1}) for ligands and uranium(VI) peroxo complexes

Compound	v(NH)	v(C–N–C)	v(C=O)	v(C=S)	v(U=O)	v(O–O)	v_{asym}(UO$_2$)	v_{sym}(UO$_2$)
MBU	2,952	1,137	1,630	–	–	–	–	–
PBU	2,940	1,117	1,631	–	–	–	–	–
MBT	2,949	1,144	–	853	–	–	–	–
PBT	2,947	1,152	–	855	–	–	–	–
MMT	2,962	1,154	–	845	–	–	–	–
PMT	2,929	1,119	–	866	–	–	–	–
MMU	2,960	1,164	1,601	–	–	–	–	–
[UO(O$_2$)MBU(NO$_3$)$_2$]	2,924	1,105	1,625	–	995	892	722	674
[UO(O$_2$)PBU(NO$_3$)$_2$]	2,923	1,111	1,629	–	1,001	891	720	668
[UO(O$_2$)MBT(NO$_3$)$_2$]	2,920	1,125	–	789	984	905	719	669
[UO(O$_2$)PBT(NO$_3$)$_2$]	2,934	1,151		740	1,002	875	719	658
[UO(O$_2$)MMT(NO$_3$)$_2$]	2,945	1,125	–	790	1,000	901	712	630
[UO(O$_2$)PMT(NO$_3$)$_2$]	2,923	1,116	–	786	989	898	734	655
[UO(O$_2$)MMU(NO$_3$)$_2$]	2,949	1,123	1,631	–	998	901	750	670

v(N–H) stretching of ligands appear at lower frequencies in the corresponding complexes [UO(O$_2$)MBU(NO$_3$)$_2$], [UO(O$_2$)PBU(NO$_3$)$_2$], and [UO(O$_2$)MMU(NO$_3$)$_2$], indicating bonding of the ligands through the carbonyl oxygen and ring nitrogen of morpholine/piperidine. Ring nitrogen atoms of alicyclic amines in a variety of ligands have been reported to coordinate metal ions [50].

In the spectra of the ligands MBT, MMT, PMT, and PBT a sharp band assigned to v(C=S) of the thioamide group and a band assigned to v(C–N–C) of the morpholine and piperidine rings are shifted to lower frequencies in the corresponding complexes [UO(O$_2$)MBT(NO$_3$)$_2$], [UO(O$_2$)MMT(NO$_3$)$_2$], [UO(O$_2$)PMT(NO$_3$)$_2$], and [UO(O$_2$)PBT(NO$_3$)$_2$] (Table 2). Another band assigned to v(N–H) stretching is also shifted to lower position in complexes compared with the free ligands. The shift of these characteristic bands of ligands to lower frequencies after complexation indicates their coordination to the metal.

In these complexes three additional bands which are not present in the spectra of free ligands are observed. Of these, a band appearing around 1,025–1,040 cm^{-1} is assigned to the bending (v_2) mode of the NO$_3$ group. Two more bands in the regions 1,425–1,465 and 1,350–1,390 cm^{-1} are assigned as the v_4 and v_1 modes, respectively, of the coordinated nitrato group. A difference in frequencies between the higher-energy bands (Δv ($v_4 - v_1$) $\approx$ 75 cm^{-1}) suggests unidentate coordination of the nitrato group [51, 52]. For bidentate coordination of a nitrato group the difference should be in the range of 120–180 cm^{-1} [53].

TGA/DTA studies

TGA and DTA thermograms were recorded up to 1,000 °C for two representative complexes [UO(O$_2$)MBU(NO$_3$)$_2$]

and [UO(O$_2$)PBT(NO$_3$)$_2$] in an atmosphere of air and nitrogen, respectively, at a heating rate of 10 °/min.

The TG curve (Fig. 1) for the complex [UO(O$_2$)MBU(NO$_3$)$_2$] in an air atmosphere shows, initially, a sharp weight loss starting from 23 to 500 °C which corresponds to a weight loss of 14.1%. This weight loss approximates to loss of peroxo and nitrate groups (theoretical weight loss 14.3%). The DTA curve of the complex contains an exothermic peak at 173 °C, confirming loss of the peroxo group as free dioxygen. Further heating up to 1,000 °C shows a gradual weight loss of 2.6% (theoretical weight loss 2.4%) attributable to loss of an oxo group. A broad exothermic curve all along indicates oxidation of the ligand.

The TG curve (Fig. 2) for the complex [UO(O$_2$)PBT(NO$_3$)$_2$] in nitrogen atmosphere shows initially a sharp weight loss starting from 25 to 500 °C which is observed to be 12.9%. This weight loss approximates to loss of nitrate and a peroxo group (theoretical weight loss 14.3%). Further heating up to 1,000 °C shows weight loss of 3.1% attributable to loss of an oxo group (theoretical weight loss 2.4%). A broad exothermic curve all along indicates oxidation of the ligand.

The TG/DTA curves of complexes of the same family, although studied in different atmospheres, show almost the same pattern of weight loss, indicating stability of the complexes.

ESI mass spectral studies

ESI mass spectra were recorded for the complexes [UO(O$_2$)MBU(NO$_3$)$_2$] (**1**) and [UO(O$_2$)PBT(NO$_3$)$_2$] (**2**). Extensive fragmentation was observed for both complexes, and only the most abundant fragment ions (with relative

Institute Instrumentation Centre, IITR, Roorkee

Sample Name: MBU-B
Data Name: HNS-2
Measurement Date: 8/23/2009   Temperature Program: Instrument: Perkin Elmer (Pyris Diamond)
Sample Weight: 11.37 mg   Cel Cel Cel/min min s   Operator: A.K.Saini
Reference Weight: 10.5 mg   Pan: Alumina
Reference Name: Alumina Powder   1*   23 1000   10   0 0.5 Atmosphere: Air (200ml/min)
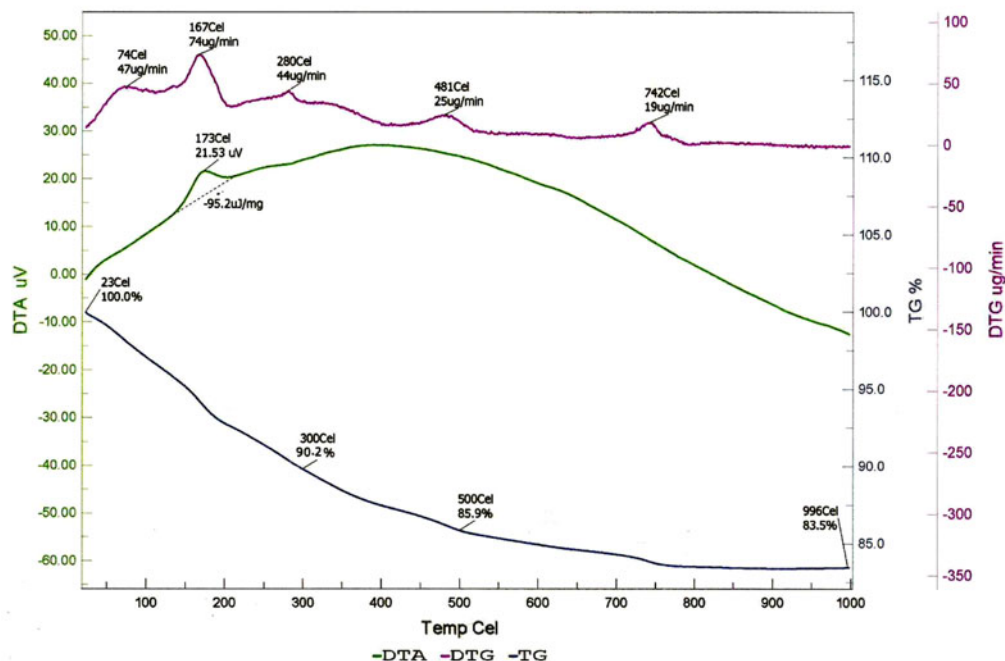
Fig. 1 TGA/DTA thermogram of [UO(O$_2$)MBU(NO$_3$)$_2$]

Institute Instrumentation Centre, IITR, Roorkee

Sample Name: PBTU-B
Data Name: HNS-1
Measurement Date: 8/23/2009   Temperature Program: Instrument: Perkin Elmer (Pyris Diamond)
Sample Weight: 11.59 mg   Cel Cel Cel/min min s   Operator: A.K.Saini
Reference Weight: 10.5 mg   Pan: Alumina
Reference Name: Alumina Powder   1*   25 1000   10   0 0.5 Atmosphere: Nitrogen (200ml/min)
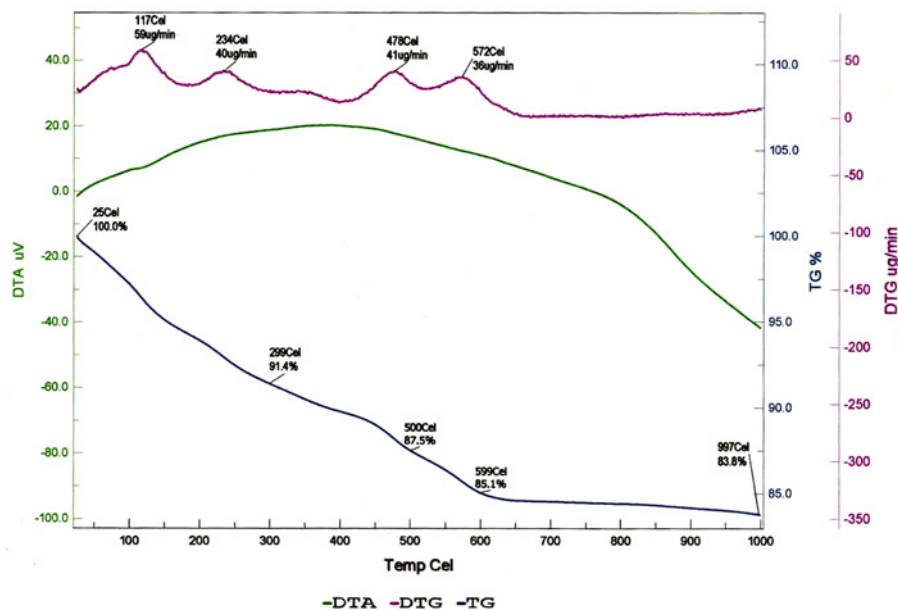
Fig. 2 TGA/DTA thermogram of [UO(O$_2$)PBT(NO$_3$)$_2$]

Table 3 Mass spectral data for uranium(VI) peroxo complexes

	m/z (%)	M − 3* (%)	M* (%)	M + 1* (%)	M + 2* (%)
Complex **1**					
$[UO(O_2)C_{12}H_{17}N_5O_8]$ (645.32 g mol^{-1})					
$[UO(O_2)C_{12}H_{17}N_5O_8]^+$	644.32 (10.07)	0.70	100	15.4	3.4
$[UOC_{12}H_{17}N_5O_8]^+$	613.32 (28.56)	0.70	100	15.4	2.9
$[UOC_{12}H_{17}N_4O_5]^+$	551.32 (0.53)	0.70	100	14.8	2.3
$[UOC_{12}H_{17}N_3O_2]^+$	489.32 (0.89)	0.70	100	14.4	1.6
$[UC_{12}H_{17}N_3O_2]^+$	473.32 (0.35)	0.70	100	14.3	1.4
$[UC_8H_9N_2O]^+$	387.32 (3.57)	0.70	100	9.5	0.6
$[UCH_2NO]^+$	282.32 (100)	0.70	100	1.5	0.2
Complex **2**					
$[UO(O_2)C_{13}H_{19}N_5O_6S]$ (659.39 g mol^{-1})					
$[UO(O_2)C_{13}H_{19}N_5O_6 S]^+$	658.39 (2.78)	0.70	100	17.2	7.8
$[UOC_{13}H_{19}N_5O_6 S]^+$	627.39 (2.22)	0.70	100	17.2	7.3
$[UOC_{13}H_{19}N_4O_3 S]^+$	565.39 (5.00)	0.70	100	16.7	6.7
$[UOC_{13}H_{19}N_3S]^+$	503.39 (12.5)	0.70	100	16.2	6.0
$[UC_{13}H_{19}N_3 S]^+$	487.39 (5.20)	0.70	100	16.1	5.8
$[UC_8H_9N_2 S]^+$	403.39 (4.44)	0.70	100	10.3	5.0
$[UCH_2NS]^+$	298.39 (100)	0.70	100	2.3	4.5

isotopic abundance) are given in Table 3. The molecular ion peak for complex **1** was at $m/z = 644.32$ for the fragment $[UO(O_2)C_{12}H_{17}N_5O_8]^+$; that for complex (**2**) was at $m/z = 658.39$ for fragment $[UO(O_2)C_{13}H_{19}N_5O_6S]^+$. Masses of the fragment ions listed in Table 3 were calculated using the uranium atomic mass equal to 238.05 amu. For complex **1** the base peak appears at $m/z = 282.32$ corresponding to $[UCH_2NO]^+$ and for complex **2** it appears at $m/z = 298.39$ corresponding to $[UCH_2NS]^+$.

Uranium has two isotopes having atomic masses of 235 and 238 amu. Their relative abundances are 0.70 and 100%, respectively. Here, the most intense isotope peak is set to 100% and percentages for the other isotope peaks are computed relative to this (Table 3). The molecular ion and fragment peaks containing uranium appear as doublets at M^{+*} and $M - 3^{+*}$, and the ratios of their relative intensities confirm the presence of the U-235 and U-238 isotopes in the fragments. In addition $M + 1^{+*}$ and $M + 2^{+*}$ peaks also appear because of the isotopic contribution of C, H, N, O, and S atoms.

Electronic spectral studies

The electronic spectra of the metal complexes in the UV–visible region (Table 4) were recorded in DMF solution at a concentration of 10^{-3} M. The spectra show three transitions in the ranges 297–335, 345–367, and 373–398 nm ascribed to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and the charge-transfer transitions from uranyl oxygen → uranium, i.e.

LMCT, $\pi O_2^{2-} \rightarrow U$ [48, 54]. There was no evidence of any d–d transition. This result is consistent with the presence of the uranium(VI) system in the complexes.

^{1}H NMR studies

The ^{1}H NMR spectrum of the representative ligand MMU was recorded in deuterated ethanol whereas that of complex was recorded in deuterated DMF solution. The spectrum of the ligand contains a triplet at $\delta = 2.37$ ppm for N–CH$_2$ of the morpholine ring and a triplet at 3.67 ppm for O–CH$_2$ of the morpholine ring. The methylidine protons of the H–CH–NH group appear as a doublet at 4.23 ppm. For the complex $[UO(O_2)MMU(NO_3)_2]$ the peaks corresponding to the four protons of the –CH$_2$ groups of N–CH$_2$ in the morpholine ring undergo a downfield shift to 2.49 ppm. This is because of coordination of the ring nitrogen of morpholine with uranium.

In a similar way, the ^{1}H NMR spectra of the ligand PMT and the complex $[UO(O_2)PMT(NO_3)_2]$ were recorded in deuterated ethanol and DMF solution, respectively. The spectrum of the ligand contains a triplet at 2.24 ppm for N–CH$_2$ of the piperidine ring. The methylidine protons of the H–CH–NH group appear at 3.72 ppm. For the complex $[UO(O_2)PMT(NO_3)_2]$ the peaks corresponding to the four protons of the –CH$_2$ groups of N–CH$_2$ in the piperidine ring undergo a downfield shift to 2.67 ppm. This, again, is because of coordination of the ring nitrogen of piperidine with uranium.

Table 4 Electronic spectral data (nm) of uranium(VI) peroxo complexes

Complex	λ/nm
[UO(O$_2$)MBU(NO$_3$)$_2$]	297, 356, 380
[UO(O$_2$)PBU(NO$_3$)$_2$]	324, 345, 375
[UO(O$_2$)MBT(NO$_3$)$_2$]	335, 367, 390
[UO(O$_2$)PBT(NO$_3$)$_2$]	321, 347, 373
[UO(O$_2$)MMT(NO$_3$)$_2$]	320, 358, 398
[UO(O$_2$)PMT(NO$_3$)$_2$]	331, 354, 395
[UO(O$_2$)MMU(NO$_3$)$_2$]	315, 357, 397

^{13}C NMR studies

The ^{13}C NMR spectra of the representative ligand MMU and the complex [UO(O$_2$)MMU(NO$_3$)$_2$] were recorded in deuterated ethanol and deuterated DMF solution, respectively. The ^{13}C spectrum of the ligand MMU contains four peaks indicating four types of carbon atom. A peak at $\delta = 162.7$ ppm is assigned to –NHCONH$_2$ and another peak at 65.7 ppm is attributed to –NH–CH$_2$–N<. The methylene carbon atoms of the morpholine ring appear at 50.4 and 66.5 ppm. In the complex [UO(O$_2$)MMU(NO$_3$)$_2$] the ring methylene carbon atoms linked to the nitrogen atom are shifted downfield to 52.6 ppm. The carbonyl carbon is also shifted downfield (165.1 ppm) because of coordination of the ligand to the metal through the carbonyl oxygen and ring nitrogen.

In a similar way the ^{13}C NMR spectrum of the representative ligand PMT and the complex [UO(O$_2$)PMT (NO$_3$)$_2$] were recorded in deuterated ethanol and deuterated DMF solution, respectively. The ^{13}C spectrum of the ligand PMT contains five peaks indicating five types of carbon atom. A peak at 182.6 ppm is assigned to –NHCSNH$_2$ and another peak at 70.8 ppm is attributed to –NH–CH$_2$–N<. The methylene carbon atoms of the piperidine ring appear at 52.3, 25.6, and 25.9 ppm. In the complex [UO(O$_2$) PMT(NO$_3$)$_2$] the ring methylene carbon atoms linked to the nitrogen atom are shifted downfield to 54.5 ppm. The thiocarbonyl carbon is also shifted downfield (185.0 ppm) because of coordination of the ligand to the metal through the thiocarbonyl sulfur and ring nitrogen.
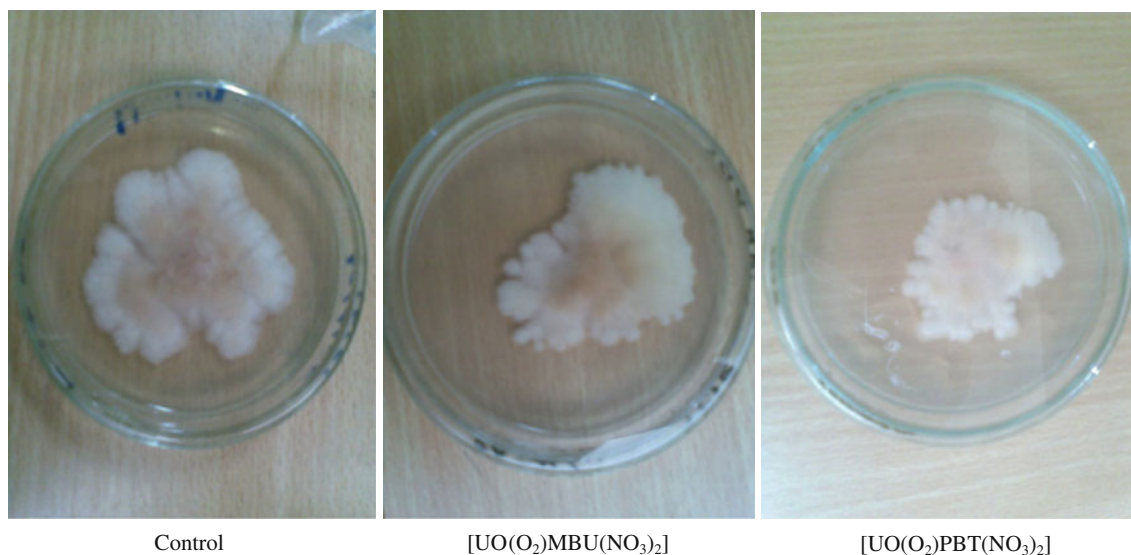
Antifungal activity

Antifungal screening of the ligands and their uranium peroxo complexes against the pathogen *Fusarium vasinfectum* was carried out using potato dextrose agar (PDA) nutrient as the medium. Zones developed on the plates were measured by measuring the diameter of the inhibited zone in millimeters. The zone of inhibition values are presented in Table 5. It is evident from the table that the metal chelates are more active than the free ligands. It is observed that on increasing the concentration of the complexes, the colony diameter of the fungus decreases and hence percentage inhibition increases compared with the corresponding ligands. From these findings it seems the prolonged activity of the complexes against the chosen organism, compared with that of the free ligand, might be because of diffusion of the metal complexes as a whole through the cell membrane or because of the combined effect of the metal and ligand. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept [55] and Tweedy's chelation theory [56]. According to Overtone's concept of cell permeability, the membrane that surrounds the cell favours the passage of only lipid-soluble materials which control antimicrobial activity. On chelation, the polarity of the metal ion is substantially reduced. This is because of overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further it increases the delocalisation of electrons over the whole chelate ring and enhances the lipophilic character of the metal complexes [57]. This increased lipophilicity leads to breakdown of the permeability barrier and enables the complexes to penetrate into the lipid membrane.

Table 5 In vitro efficacy of complexes against *Fusarium vasinfectum*

Complex	Colony diameter (mm) at 100 ppm		%Inhibition $I = [(C − T)/C] \times 100$ at 100 ppm		Colony diameter (mm) at 200 ppm		%Inhibition I at 200 ppm	
	Ligand	Complex	Ligand	Complex	Ligand	Complex	Ligand	Complex
[UO(O$_2$)MBU(NO$_3$)$_2$]	48	39	36	48	37	28	51	63
[UO(O$_2$)PBU(NO$_3$)$_2$]	42	35	44	53	32	25	57	67
[UO(O$_2$)MBT(NO$_3$)$_2$]	49	38	35	49	36	29	52	61
[UO(O$_2$)PBT(NO$_3$)$_2$]	43	36	43	52	33	26	56	65
[UO(O$_2$)MMT(NO$_3$)$_2$]	41	32	45	57	35	27	53	64
[UO(O$_2$)PMT(NO$_3$)$_2$]	47	37	37	51	40	22	47	71
[UO(O$_2$)MMU(NO$_3$)$_2$]	45	39	40	48	39	23	48	69

Colony diameter of control $C = 75$ mm

Control   [UO(O$_2$)MBU(NO$_3$)$_2$]   [UO(O$_2$)PBT(NO$_3$)$_2$]

Fig. 3 Antifungal activity against *Fusarium vasinfectum* of complexes at 100 ppm
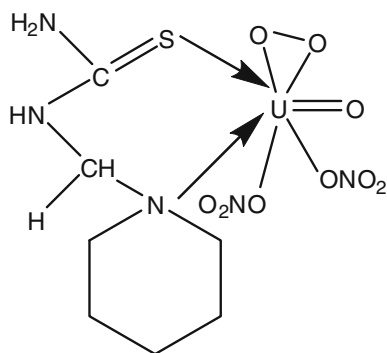
Scheme 2

The antifungal activity of [UO(O$_2$)MBU(NO$_3$)$_2$] and [UO(O$_2$)PBT(NO$_3$)$_2$] is shown in Fig. 3.

On the basis of analytical, IR, UV–Vis, and mass spectral data, pentagonal bipyramidal geometry was proposed. A representative structure for the complex [UO(O$_2$)PMT(NO$_3$)$_2$] is given in Scheme 2.

Experimental

Materials and physical measurements

All reagents used were chemically pure and analytical-reagent grade. Solvents used were purified and dried according to standard procedures [58]. Morpholine (Ranbaxy), piperidine (SDS), benzaldehyde (Ranbaxy), urea (Rankem), thiourea (NICE), formaldehyde (Ranbaxy), uranyl nitrate (SISCO), and hydrogen peroxide (Merck) were used as supplied. Analysis of uranium was carried out gravimetrically as uranyl oxinate UO$_2$(C$_9$H$_6$ON)$_2$C$_9$H$_7$ON

after decomposing the complex with concentrated nitric acid [58]. Carbon, hydrogen, and nitrogen were analysed microanalytically by use of a Leco model 932 CHNS analyser; results agreed favourably with calculated values. The total peroxide content of the complexes was determined by adding a weighed amount of the compound to a cold solution of 1.5% (*w/v*) boric acid in 0.7 M sulfuric acid (100 cm^3) and then titrating with standard cerium(IV) solution [59]. Molar conductivity of the complexes was measured at room temperature, by use of a model 611E digital conductivity metre with a conductivity cell with a cell constant of 1.0 ± 10%, using 10^{-3} molar solutions of the complexes in DMF. Magnetic susceptibility measurements were carried out by Gouy's method at room temperature using Hg[Co(NCS)$_4$] as standard. IR spectra of the complexes over the region 4,000–400 cm^{-1} were recorded on a Perkin–Elmer FT-IR model RX1 spectrophotometer, using KBr discs. Melting points were determined on an Analab melting point apparatus and mass spectral data were obtained on a ESI-Esquire 3000 Bruker Daltonics spectrometer. Electronic spectra over the region 200–900 nm were recorded by use of a Systronics UV–visible single-beam spectrophotometer, using 10^{-3} M DMF solutions of the complexes. TGA/DTA studies were recorded on a Linseis STA PT-1000 (Pyris Diamond) thermoanalyser at a heating rate of 10°/min in atmospheres of air and nitrogen in the temperature range 23–1,000 °C.

Preparation of ligands

The ligands MBU, PBU, MBT, PBT, MMT, PMT, and MMU were prepared by the reported method [60]. In a typical reaction urea/thiourea (0.1 mol) in 20 cm^3 ethanol

was mixed with piperidine/morpholine (0.1 mol) with constant stirring to obtain a clear solution under cooling with ice. To the resulting solution, benzaldehyde/formaldehyde (0.1 mol) was added dropwise with stirring for 15–20 min under cooling with ice. The reaction mixture was then kept at room temperature for two days. The colourless solid obtained was filtered, washed with distilled water, and recrystallized from ethanol. The melting points of the ligands MBU, PBU, MBT, PBT, MMT, PMT, and MMU were 68, 69, 74, 72, 141, 120 and 162 °C, respectively. These values are identical with the values reported for the ligands in the literature [60].

Preparation of uranyl peroxo complexes

The peroxo complexes were synthesized by a reported procedure [61]. In a typical reaction 0.502 g $UO_2(NO_3)_2 \cdot 6H_2O$ (1 mmol) was dissolved in methanol. An equimolar (1 mmol) methanolic solution (30 cm^3) of the ligand (Mannich base) was added to the uranyl nitrate solution followed by addition of 0.1122 g potassium hydroxide (2 mmol). The solution was heated under reflux for 15 min, then 10 cm^3 30% H_2O_2 was added dropwise and heated under reflux for another hour. After cooling, the resulting yellow precipitates were isolated by filtration and washed successively with methanol and ether and dried in vacuo.

Dinitrouranylperoxomorpholinobenzylurea ([$UO(O_2)MBU(NO_3)_2$], **1**, $UC_{12}H_{17}N_5O_{11}$) Analytical data are given in Tables 1, 2, 3, and 4.

Dinitrouranylperoxopiperidinobenzylurea: ([$UO(O_2)PBU(NO_3)_2$], **2**, $UC_{13}H_{19}N_5O_{11}$) Analytical data are given in Tables 1, 2, 3, and 4.

Dinitrouranylperoxomorpholinobenzylthiourea ([$UO(O_2)MBT(NO_3)_2$], **3**, $UC_{12}H_{17}N_5O_{11}S$) Analytical data are given in Tables 1, 2, 3, and 4.

Dinitrouranylperoxopiperidinobenzylthiourea ([$UO(O_2)PBT(NO_3)_2$], **4**, $UC_{13}H_{19}N_5O_9S$) Analytical data are given in Tables 1, 2, 3, and 4.

Dinitrouranylperoxomorpholinomethylthiourea ([$UO(O_2)MMT(NO_3)_2$], **5**, $UC_6H_{13}N_5O_{10}S$) Analytical data are given in Tables 1, 2, 3, and 4.

Dinitrouranylperoxopiperidinomethylthiourea ([$UO(O_2)PMT(NO_3)_2$], **6**, $UC_7H_{15}N_5O_9S$) Analytical data are given in Tables 1, 2, 3, and 4.

Dinitrouranylperoxomorpholinomethylurea ([$UO(O_2)MMU(NO_3)_2$], **7**, $UC_6H_{13}N_5O_{11}$) Analytical data are given in Tables 1, 2, 3, and 4.

Antimicrobial study

The in-vitro biological effects of the compounds against the pathogen *Fusarium vasinfectum* (Table 5) were tested by the poisoned food method using PDA nutrient as the medium. The test solutions were prepared by dissolving the compounds in DMF. PDA mixed with test solution was poured into sterilized Petri dishes. After solidification, the plates were inoculated with a seven-day-old culture of the pathogen by placing 2-mm sample in the centre of plates. The inoculated plates were incubated at 27 °C for 4 days. The linear growth of the fungus on control and treated plates was recorded for different concentrations of the complexes. Inhibition of the growth of *Fusarium vasinfectum* compared with control was calculated in accordance with Vincent [62]:

$$\%\text{Inhibition } (I) = [(C - T)/C] \times 100$$

where I is percentage inhibition, C is the growth of the fungus (mm) on control plates, and T is the growth of the fungus (mm) on treated plates.

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