REVIEW ARTICLE
ISSN 2249 - 2119

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Ram Agarwal *et al.*
Int. J. Chem.
Vol 1 (4) (2012) : pp 576 - 597

A review of high coordination compounds of dioxouranium(VI) derived from Schiff bases of 4-aminoantipyrine

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Abstract
Uranium(VI) is very prominent in its complexation tendency, especially when it forms compounds exhibiting high coordination numbers. A metal acquires a high coordination number when (a) it is a small and highly charged ion with suitable vacant orbital of right energy, (b) it can attain a noble gas structure (effective atomic rule), and (c) it can attain a symmetrical shape and high CFSE in complex. U(VI) ion has positive charge which is one of the essential conditions for high coordination, as it will not allow the negative charge donated by electrons from the ligands to accumulate on the central metal ion. U^{6+} successfully reveals high coordination numbers 6 to 10. The examples of different coordination numbers of UO_2^{2+} coordination compounds are available in literature, many of which have been reported from our laboratory. We have synthesized and reported a number of high coordinated complexes of UO_2^{2+} with Schiff bases. All the coordination compounds reported herein have been suitably characterized by various physico-chemical techniques. The present review summarizes mostly our work on the UO_2^{2+} complexes of Schiff bases 4-aminoantipyrine, including 4-aminoantipyrine derived semicarbazones, thiosemicarbazones and some mixed ligand complexes.

Keywords: *Dioxouranium(VI) complexes, Schiff bases, 4-Aminoantipyrine, Coordination number.*

Introduction

Uranium(VI) belongs to the actinide series and unlike the lanthanides in which the 4*f*-electrons are not accessible for bonding, the 5*f*-orbitals of the actinides extend spatially into the outer valency regions of the atoms. The 5*f*-orbitals are less effectively shielded by the outer electrons and have relatively lower binding energies, than is the case with the 4*f*-orbitals. Due to these factors the actinides, in marked contrast to the lanthanides, form a wide variety of complexes in which hybridization normally involve the unoccupied higher energy orbitals (6*d*, 7*s*, 7*p*), which can only be expected with strong coordinating ligands[1-6]. Thus such stable complexes, other than the hydrated cations in solution, are found most commonly with ligands which contain highly

electronegative donor atoms such as oxygen and nitrogen[2-4,6]. Although *f*-orbitals are obviously not as important as *d*-orbitals in bonding, the contribution of the former to binding cannot be neglected. For example, the stability of the oxygenated ions MO_2^+ and MO_2^{2+} is attributed to *f*-orbital participation[7].

Dioxouranium ion, UO_2^{2+}, is quite peculiar both in its structure and in its coordination chemistry. From a geometric point of view UO_2^{2+} can be considered as a single species. Since coordination occurs in the plane normal to the O-U-O axis, the number of ligands in the equatorial plane can easily be up to six. In other words, UO_2^{2+} can coordinate with 2 to 6 other atoms, ions or molecules in the equatorial plane with a strong tendency to make these ligating atoms coplanar. Thus the actinide metals, especially uranium(VI) has attracted a greater interest because of the formation of a variety of coordination compounds with varying coordination numbers[1-6,8-12]. There are a large number of geometric structures of uranium(VI) complexes which are generally not found in the usual coordination chemistry of *d*-block transition metal ions. This peculiarity of uranium(VI) complexes have been of great interest not only from a speculative point of view but also because of their various applications involving the technology and uses of uranium derivatives. Therefore the complexing ability of dioxouranium(VI) have been investigated with a wide variety of organic and inorganic ligands[1-6,8-13].

In its hexavalent form, uranium usually exists in the environment as the uranyl dication, UO_2^{2+}, which forms highly soluble complexes with a variety of anionic species including fluoride, chloride, carbonate, nitrate, sulfate, phosphate, silicate and acetate; commonly increasing the solubility of U in environment which causes environmental concern. However, Schiff base uranyl complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer, herbicidal and analytical applications[1,13-18]. Nitrogen-containing ligands such as Schiff bases and their metal complexes have played an important role in the development of coordination chemistry resulting in enormous publi-cations, ranging from pure synthetic work to physico-chemical and biochemically relevant studies of metal complexes and found wide range of applications. In the most recent study, Ghammamy and Sedaghathas reported the synthesis, characterization and antitumor properties of a number of the ligands and uranyl complexes[1]. Some derivatives of semicarbazones or hydrazones have been used for the spectrophotometric determination of UO_2^{2+} including other metal ions[13-15]. Albe and Olivahas reported the complexation reaction of uranium(VI) with salicylaldehyde semicarbazone for its determination at part per billion levels[14]. Most recently, Lokhande *et al.* has developed a selective and sensitive spectrophotometric method for the determination of uranium(VI) using acetophenone 2',5'-dihydroxy semicarbazone as an extractive reagent[15]. The amount of uranium present in the organic phase determined quantitatively by spectrophotometric method by taking absorbance at 380 nm and that in the aqueous phase was determined by oxine method[15]. In addition, due to the absorption and luminescence spectral properties, and excited-state electron-transfer properties of the UO_2^{2+} ion, dioxouranium(VI) complexes have possible applications in solar energy conversion systems[16,17]. The complexation tendency of polymer supported calix[4]arene-semicarbazone derivative has also been used for the separation and the preconcentration of La(III), Ce(III), Th(IV) and U(VI) from their binary and ternary mixtures[18].

Considering the potential applications of dioxouranium(VI) complexes, many efforts have been directed towards the synthesis and the characterization of novel uranyl complexes[1-6,8-13,19]. The complexes of the uranyl ion, UO_2^{2+}, are of special interest as they show flexible coordination geometries[16]. In general, the coordination number of uranium(VI) varies from 6 to 10 in dioxouranium(VI) complexes[8]. However, coordination number 14 has also been reported in the literature for dioxouranium(VI) complexes[10]. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition and inner-transition metals. They show interesting properties *e.g.*, their ability to bind oxygen[20], catalytic activity in hydrogenation of olefin[21], transfer of

an amino group[22], photochromic properties[23] and complexing ability towards toxic metals[24]. The interest of studying Schiff bases containing O, N, S-donor arose from their significant antifungal, antibacterial and anticancer activities[25]. Especially, Schiff base complexes of uranium(VI) have aroused interest on account of their stability, high coordination numbers and usefulness in selective chemical separations[13,18]. Uranyl complexes of ligands with O and N donors have been reviewed and quite a few complexes of hydrazone Schiff bases have also been reported[13,17]. The importance of actinides compounds has been depicted by the most recent publication of an excellent review on lanthanides and actinides: annual survey of their organometallic chemistry covering the year 2009 and 2010 by Edelmann[26]. We have specifically been interested in the synthetic and structural chemistry of the uranyl dication, UO_2^{2+}, and the *f*-elements (*vide infra*)[2,10,27]. As part of our systematic and characterization studies on the coordination complexes of the lanthanide and actinide elements, we have extensively published (*vide infra*) on the structural chemistry of semicarbazone, thiosemicarbazone and mixed ligand complexes[2,10,27] and very recently reported a review on lanthanide coordination compounds[27]. In continuation of our interest in uranyl(VI) complexes, in the present review we report the summary of the research work mostly carried out in our laboratory on uranyl(VI) complexes of Schiff bases derived from 4-amino-antipyrine, semicarbazone and thiosemicarbazone derivatives of 4-aminoantipyrine and some mixed ligand complexes of uranyl(VI)-semicarbazones as primary ligand and sulphoxide as secondary ligand.

Uranyl(VI) Complexes of Schiff Bases of 4-Aminoantipyrine

4-Aminoantipyrine (Figure 1) forms a number of Schiff bases with aldehydes/ketones and are reported to be excellent reagents for biological, pharmacological, clinical and analytical applications[28]. 4-Aminoantipyrine *i.e.* 1-phenyl-2,3-dimethyl-4-amino-5-pyrazolone has a N-phenyl group and thus resembles N-substituted amides. Coordination chemists, medicinal chemists and analytical chemists have extensively studied 4-aminoantipyrine complexes. Many researchers have published on metal complexes of 4-aminoantipyrine based derivatives[29-34]. The majority of the Schiff bases of 4-aminoantipyrine derivatives are obtained in good yield through its condensation reaction with aryl aldehydes, ketones, semicarbazides, thiosemicarbazides, etc. in aqueous or alcoholic solution[30,35]. In literature, a number of reports on transition metal complexes of Schiff bases of 4-aminoantipyrine are reported, which however have not focused on dioxouranium(VI) complexes of Schiff bases

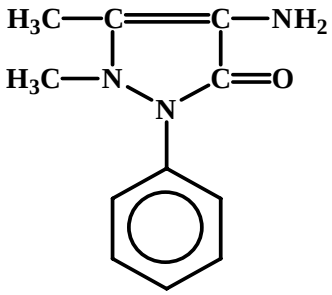

Fig. 1. Structure of 4-aminoantipyrine

derived from 4-aminoantipyrine[27]. However, we have synthesized and reported a number of Schiff bases derived from 4-aminoantipyrine[36-44] *viz.*, 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrine (HNAAP), 4[N-(3'-methoxybenzalidene)amino]antipyrine (MBAAP), 4[N-(3',4',5'-trimethoxybenzalidene)amino]antipyrine (TMBAAP), 4[N-(4'-dimethylaminobenzalidene)-amino]antipyrine (DABAAP), 4[N-(4'-hydroxy-3'-methoxybenzalidene)amino]antipyrine (HMBAAP), 4[N-(2'-nitrobenzalidene)amino]antipyrine (2'-NO_2BAAP), 4[N-(3'-nitrobenzalidene)amino]antipyrine (3'-NO_2BAAP), 4[N-(cinnamalidene)amino]antipyrine (CAAP), 4[N-(salicylicdene)amino]antipyrine (SAAP), 4[N-(benzalidene)amino]antipyrine (BAAP), 4[N-(furfural)amino]antipyrine (FFAAP) (Figures 2-12).

The reaction of dioxouranium(VI) salts with HNAAP, MBAAP, TMBAAP, DABAAP, HMBAAP, 2'-NO_2BAAP, 3'-NO_2BAAP, CAAP, SAAP, BAAP and FFAAP in non-aqueous solvents resulted in the formation of complexes with the general composition $UO_2X \cdot nL$ (n = 2, X = SO_4) or $UO_2X_2 \cdot nL$ (n = 2, X = Cl, Br, I, NCS, OAc, NO_3; n = 3, X = ClO_4; L = HNAAP, MBAAP,

TMBAAP, DABAAP, HMBAAP, 2'-NO_2BAAP, 3'-NO_2BAAP, CAAP, SAAP, BAAP or FFAAP)[45-49]. These dioxouranium(VI) complexes of Schiff bases, semicarbazones/thiosemicarbazones derived from 4-aminoantipyrine are given in Table 1[36-49]. The conductance measurements in nitrobenzene suggest the non-electrolytic behaviour of chloro, bromo, iodo, thiocyanato, nitrato, acetato and sulphato complexes, while the perchlorato complexes dissociate in this solvent and behave as 1:2 electrolytes. The cryoscopic determination of molecular weight in freezing nitrobenzene are in broad agreement with the conductance data. On the basis of physico-chemical studies, we have formulated all these complexes as $[UO_2(L)_2X_2]$ (X = Cl, Br, I, NCS, OAc, NO_3), $[UO_2(L)_2SO_4]$ and $[UO_2(L)_3](ClO_4)_2$[36-49].

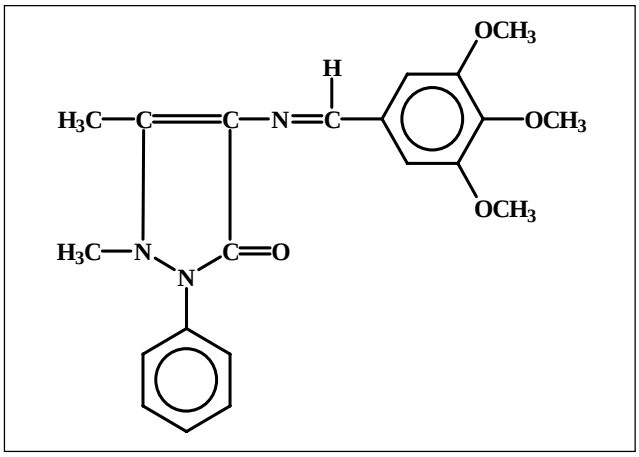

Fig. 4. Structure of 4[N-(3',4',5'-trimethoxybenzalidene)amino]antipyrine (TMBAAP)

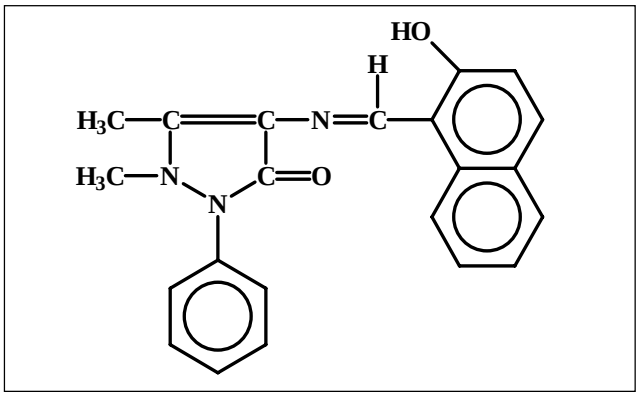

Fig. 2. Structure of 4[(N-(2'-hydroxy-1'-naphthalidene)amino]antipyrine (HNAAP)

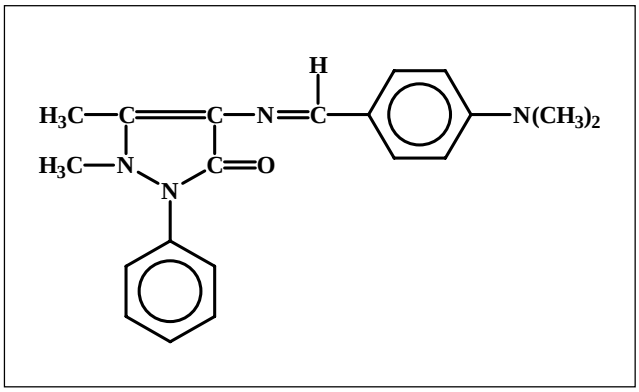

Fig. 5. Structure of 4[(N-(4'-dimethylamino-benzalidene)amino]antipyrine (DABAAP)

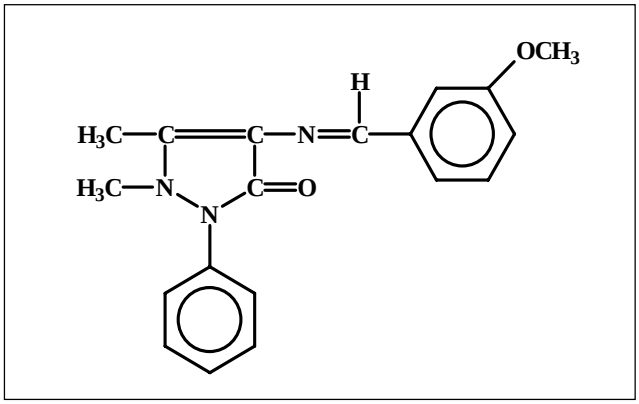

Fig. 3. Structure of 4[(N-(3'-methoxy-benzalidene)amino]antipyrine (MBAAP)

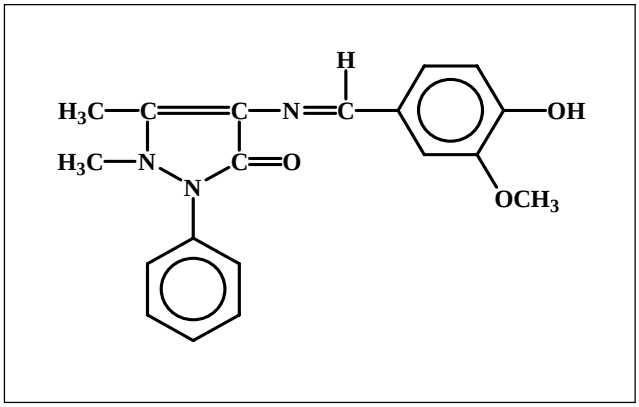

Fig. 6. Structure of 4[(N-(4'-hydroxy-3'-methoxy-benzalidene)amino]antipyrine (HMBAAP)

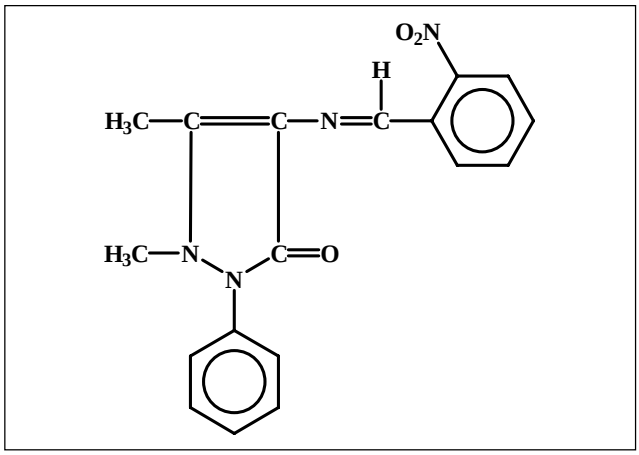

Fig. 7. Structure of 4[N-(2'-nitro-benzalidene)amino]antipyrine (2'-NO_2BAAP)

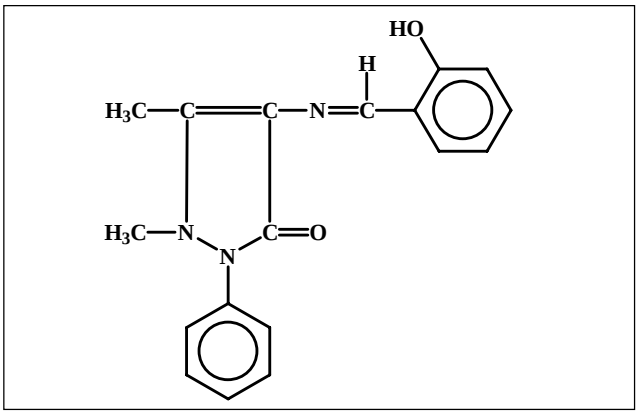

Fig. 10. Structure of 4[N-(salicylicdene)amino]antipyrine (SAAP)

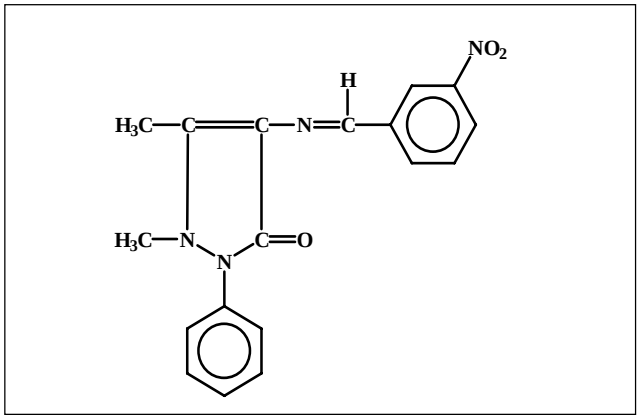

Fig. 8. Structure of 4[N-(3'-nitro-benzalidene)amino]antipyrine (3'-NO_2BAAP)

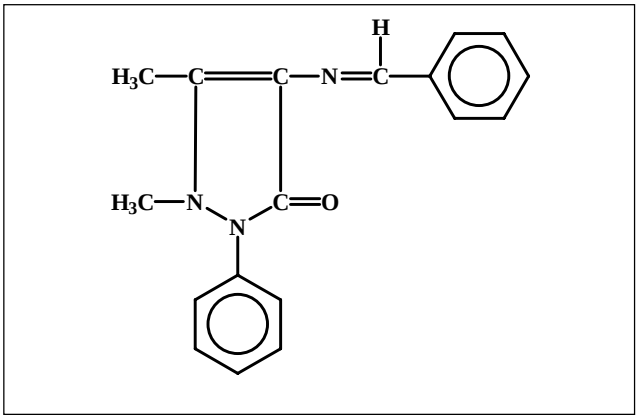

Fig. 11. Structure of 4[N-(benzalidene)amino]antipyrine (BAAP)

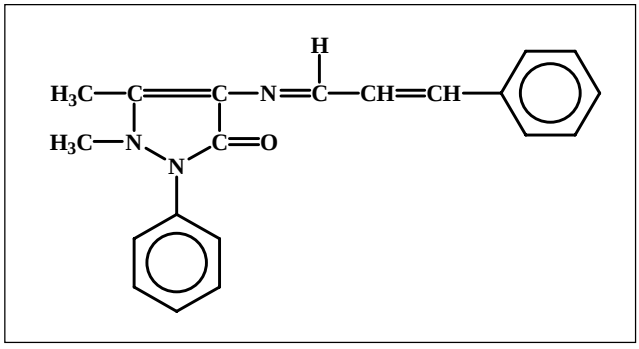

Fig. 9. Structure of 4[(N-(cinnamalidene)amino]-antipyrine (CAAP)

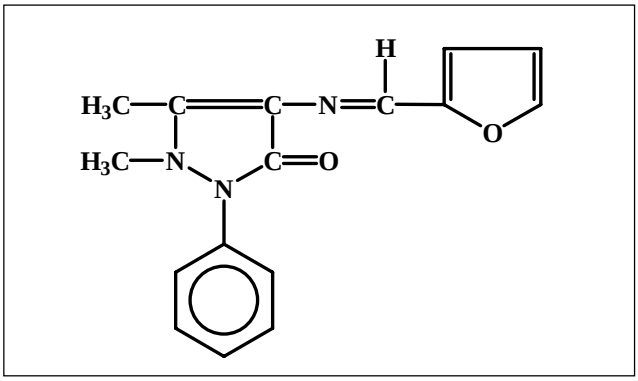

Fig. 12. Structure of 4[(N-(furfural)amino]antipyrine (FFAAP)

Table 1. Dioxouranium(VI) complexes of Schiff bases, semicarbazones/thiosemicarbazones derived from 4-aminoantipyrine.

Lewis acid	Ligand	Composition of the complexes	Physico-chemical studies	Coord. no.	Reference
UO_2Cl_2	HNAAP	$[UO_2(HNAAP)_2Cl_2]$	Elemental analysis, molar conductance, molar mass, infrared and thermogravimetric analysis	8	36
UO_2Br_2	HNAAP	$[UO_2(HNAAP)_2Br_2]$	--do--	8	36
UO_2I_2	HNAAP	$[UO_2(HNAAP)_2I_2]$	--do--	8	36
$UO_2(NO_3)_2$	HNAAP	$[UO_2(HNAAP)_2(NO_3)_2]$	--do--	10	36
$UO_2(NCS)_2$	HNAAP	$[UO_2(HNAAP)_2(NCS)_2]$	--do--	8	36
$UO_2(ClO_4)_2$	HNAAP	$[UO_2(HNAAP)_3](ClO_4)_2$	--do--	8	36
$UO_2(OAc)_2$	HNAAP	$[UO_2(HNAAP)_2(OAc)_2]$	--do--	10	36
UO_2Cl_2	MBAAP	$[UO_2(MBAAP)_2Cl_2]$	--do--	8	37
UO_2Br_2	MBAAP	$[UO_2(MBAAP)_2Br_2]$	--do--	8	37
UO_2I_2	MBAAP	$[UO_2(MBAAP)_2I_2]$	--do--	8	37
$UO_2(NO_3)_2$	MBAAP	$[UO_2(MBAAP)_2(NO_3)_2]$	--do--	10	37
$UO_2(NCS)_2$	MBAAP	$[UO_2(MBAAP)_2(NCS)_2]$	--do--	8	37
$UO_2(ClO_4)_2$	MBAAP	$[UO_2(MBAAP)_3](ClO_4)_2$	--do--	8	37
$UO_2(OAc)_2$	MBAAP	$[UO_2(MBAAP)_2(OAc)_2]$	--do--	10	37
UO_2Cl_2	TMBAAP	$[UO_2(TMBAAP)_2Cl_2]$	--do--	8	38
UO_2Br_2	TMBAAP	$[UO_2(TMBAAP)_2Br_2]$	--do--	8	38
UO_2I_2	TMBAAP	$[UO_2(TMBAAP)_2I_2]$	--do--	8	38
$UO_2(NO_3)_2$	TMBAAP	$[UO_2(TMBAAP)_2(NO_3)_2]$	--do--	10	38
$UO_2(NCS)_2$	TMBAAP	$[UO_2(TMBAAP)_2(NCS)_2]$	--do--	8	38
$UO_2(ClO_4)_2$	TMBAAP	$[UO_2(TMBAAP)_3](ClO_4)_2$	--do--	8	38
$UO_2(OAc)_2$	TMBAAP	$[UO_2(TMBAAP)_2(OAc)_2]$	--do--	10	38
UO_2Br_2	DABAAP	$[UO_2(DABAAP)_2Br_2]$	--do--	8	39
UO_2I_2	DABAAP	$[UO_2(DABAAP)_2I_2]$	--do--	8	39
$UO_2(NO_3)_2$	DABAAP	$[UO_2(DABAAP)_2(NO_3)_2]$	--do--	10	39
$UO_2(NCS)_2$	DABAAP	$[UO_2(DABAAP)_2(NCS)_2]$	--do--	8	39
$UO_2(ClO_4)_2$	DABAAP	$[UO_2(DABAAP)_3](ClO_4)_2$	--do--	8	39
$UO_2(OAc)_2$	DABAAP	$[UO_2(DABAAP)_2(OAc)_2]$	--do--	10	39
UO_2Br_2	HMBAAP	$[UO_2(HMBAAP)_2Br_2]$	--do--	8	40
UO_2I_2	HMBAAP	$[UO_2(HMBAAP)_2I_2]$	--do--	8	40
$UO_2(NO_3)_2$	HMBAAP	$[UO_2(HMBAAP)_2(NO_3)_2]$	--do--	10	40
$UO_2(NCS)_2$	HMBAAP	$[UO_2(HMBAAP)_2(NCS)_2]$	--do--	8	40
$UO_2(ClO_4)_2$	HMBAAP	$[UO_2(HMBAAP)_3](ClO_4)_2$	--do--	8	40
$UO_2(OAc)_2$	HMBAAP	$[UO_2(HMBAAP)_2(OAc)_2]$	--do--	10	40
UO_2Br_2	2'-NO_2BAAP	$[UO_2(2'\text{-}NO_2BAAP)_2Br_2]$	--do--	8	40
UO_2I_2	2'-NO_2BAAP	$[UO_2(2'\text{-}NO_2BAAP)_2I_2]$	--do--	8	40
$UO_2(NO_3)_2$	2'-NO_2BAAP	$[UO_2(2'\text{-}NO_2BAAP)_2(NO_3)_2]$	--do--	10	40
$UO_2(NCS)_2$	2'-NO_2BAAP	$[UO_2(2'\text{-}NO_2BAAP)_2(NCS)_2]$	--do--	8	40

$UO_2(ClO_4)_2$	2'-NO_2BAAP	$[UO_2(2'\text{-}NO_2BAAP)_3](ClO_4)_2$	--- do--	8	40
$UO_2(OAc)_2$	2'-NO_2BAAP	$[UO_2(2'\text{-}NO_2BAAP)_2(OAc)_2]$	--do--	10	40
UO_2Br_2	3'-NO_2BAAP	$[UO_2(3'\text{-}NO_2BAAP)_2Br_2]$	--do--	8	40
UO_2I_2	3'-NO_2BAAP	$[UO_2(3'\text{-}NO_2BAAP)_2I_2]$	--do--	8	40
$UO_2(NO_3)_2$	3'-NO_2BAAP	$[UO_2(3'\text{-}NO_2BAAP)_2(NO_3)_2]$	--do--	10	40
$UO_2(NCS)_2$	3'-NO_2BAAP	$[UO_2(3'\text{-}NO_2BAAP)_2(NCS)_2]$	--do--	8	40
$UO_2(ClO_4)_2$	3'-NO_2BAAP	$[UO_2(3'\text{-}NO_2BAAP)_3](ClO_4)_2$	--do--	8	40
$UO_2(OAc)_2$	3'-NO_2BAAP	$[UO_2(3'\text{-}NO_2BAAP)_2(OAc)_2]$	--do--	10	40
UO_2Br_2	CAAP	$[UO_2(CAAP)_2Br_2]$	--do--	8	41
UO_2I_2	CAAP	$[UO_2(CAAP)_2I_2]$	--do-- and XRD	8	41
$UO_2(NO_3)_2$	CAAP	$[UO_2(CAAP)_2(NO_3)_2]$	--do--	10	41
$UO_2(NCS)_2$	CAAP	$[UO_2(CAAP)_2(NCS)_2]$	--do--	8	41
$UO_2(ClO_4)_2$	CAAP	$[UO_2(CAAP)_3](ClO_4)_2$	--do--	8	41
$UO_2(OAc)_2$	CAAP	$[UO_2(CAAP)_2(OAc)_2]$	--do--	10	41
UO_2Br_2	SAAP	$[UO_2(SAAP)_2Br_2]$	--do--	8	41
UO_2I_2	SAAP	$[UO_2(SAAP)_2I_2]$	--do--	8	41
$UO_2(NO_3)_2$	SAAP	$[UO_2(SAAP)_2(NO_3)_2]$	--do--	10	41
$UO_2(NCS)_2$	SAAP	$[UO_2(SAAP)_2(NCS)_2]$	--do--	8	41
$UO_2(ClO_4)_2$	SAAP	$[UO_2(SAAP)_3](ClO_4)_2$	--do--	8	41
$UO_2(OAc)_2$	SAAP	$[UO_2(SAAP)_2(OAc)_2]$	--do--	10	41
UO_2Br_2	BAAP	$[UO_2(BAAP)_2Br_2]$	--do--	8	42
UO_2I_2	BAAP	$[UO_2(BAAP)_2I_2]$	--do--	8	42
$UO_2(NO_3)_2$	BAAP	$[UO_2(BAAP)_2(NO_3)_2]$	--do--	10	42
$UO_2(NCS)_2$	BAAP	$[UO_2(BAAP)_2(NCS)_2]$	--do--	8	42
$UO_2(ClO_4)_2$	BAAP	$[UO_2(BAAP)_3](ClO_4)_2$	--do--	8	42
$UO_2(OAc)_2$	BAAP	$[UO_2(BAAP)_2(OAc)_2]$	--do--	10	42
UO_2SO_4	2'-NO_2BAAP	$[UO_2(2'\text{-}NO_2BAAP)_2SO_4]$	--do--	8	43
UO_2SO_4	3'-NO_2BAAP	$[UO_2(3'\text{-}NO_2BAAP)_2SO_4]$	--do--	8	43
UO_2SO_4	DABAAP	$[UO_2(DABAAP)_2SO_4]$	--do--	8	43
UO_2SO_4	MBAAP	$[UO_2(MBAAP)_2SO_4]$	--do--	8	43
UO_2SO_4	HMBAAP	$[UO_2(HMBAAP)_2SO_4]$	--do--	8	43
UO_2SO_4	CAAP	$[UO_2(CAAP)_2SO_4]$	--do--	8	43
UO_2SO_4	HNAAP	$[UO_2(HNAAP)_2SO_4]$	--do--	8	43
UO_2SO_4	FFAAP	$[UO_2(FFAAP)_2SO_4]$	--do--	8	43
UO_2Br_2	FFAAP	$[UO_2(FFAAP)_2Br_2]$	--do--	8	44
UO_2I_2	FFAAP	$[UO_2(FFAAP)_2I_2]$	--do--	8	44
$UO_2(NO_3)_2$	FFAAP	$[UO_2(FFAAP)_2(NO_3)_2]$	--do--	10	44
$UO_2(NCS)_2$	FFAAP	$[UO_2(FFAAP)_2(NCS)_2]$	--do--	8	44
$UO_2(ClO_4)_2$	FFAAP	$[UO_2(FFAAP)_3](ClO_4)_2$	--do--	8	44
$UO_2(OAc)_2$	FFAAP	$[UO_2(FFAAP)_2(OAc)_2]$	--do--	10	44
UO_2Br_2	BAAPS	$[UO_2(BAAPS)_2Br_2]$	--do--	10	45
UO_2I_2	BAAPS	$[UO_2(BAAPS)_2I_2]$	--do--	10	45

$UO_2(NCS)_2$	BAAPS	$[UO_2(BAAPS)_2(NCS)_2]$	--do--	10	45
$UO_2(ClO_4)_2$	BAAPS	$[UO_2(BAAPS)_2](ClO_4)_2$	--do--	8	45
$UO_2(NO_3)_2$	BAAPS	$[UO_2(BAAPS)(NO_3)_2]$	--do--	9	45
$UO_2(OAc)_2$	BAAPS	$[UO_2(BAAPS)(OAc)_2]$	--do--	9	45
UO_2Br_2	MBAAPS	$[UO_2(MBAAPS)_2Br_2]$	--do--	10	45
UO_2I_2	MBAAPS	$[UO_2(MBAAPS)_2I_2]$	--do--	10	45
$UO_2(NCS)_2$	MBAAPS	$[UO_2(MBAAPS)_2(NCS)_2]$	--do--	10	45
$UO_2(ClO_4)_2$	MBAAPS	$[UO_2(MBAAPS)_2](ClO_4)_2$	--do--	8	45
$UO_2(NO_3)_2$	MBAAPS	$[UO_2(MBAAPS)(NO_3)_2]$	--do--	9	45
$UO_2(OAc)_2$	MBAAPS	$[UO_2(MBAAPS)(OAc)_2]$	--do--	9	45
UO_2Br_2	DABAAPS	$[UO_2(DABAAPS)_2Br_2]$	--do--	10	46
UO_2I_2	DABAAPS	$[UO_2(DABAAPS)_2I_2]$	--do--	10	46
$UO_2(NCS)_2$	DABAAPS	$[UO_2(DABAAPS)_2(NCS)_2]$	--do--	10	46
$UO_2(ClO_4)_2$	DABAAPS	$[UO_2(DABAAPS)_2](ClO_4)_2$	--do--	8	46
$UO_2(NO_3)_2$	DABAAPS	$[UO_2(DABAAPS)(NO_3)_2]$	--do--	8	46
$UO_2(OAc)_2$	DABAAPS	$[UO_2(DABAAPS)(OAc)_2]$	--do--	**9**	46
UO_2Br_2	2'-NO_2BAAPS	$[UO_2(2'\text{-}NO_2BAAPS)_2Br_2]$	--do--	10	46
UO_2I_2	2'-NO_2BAAPS	$[UO_2(2'\text{-}NO_2BAAPS)_2I_2]$	--do--	10	46
$UO_2(NCS)_2$	2'-NO_2BAAPS	$[UO_2(2'\text{-}NO_2BAAPS)_2(NCS)_2]$	--do--	10	46
$UO_2(ClO_4)_2$	2'-NO_2BAAPS	$[UO_2(2'\text{-}NO_2BAAPS)_2](ClO_4)_2$	--do--	8	46
$UO_2(NO_3)_2$	2'-NO_2BAAPS	$[UO_2(2'\text{-}NO_2BAAPS)(NO_3)_2]$	--do--	9	46
$UO_2(OAc)_2$	2'-NO_2BAAPS	$[UO_2(2'\text{-}NO_2BAAPS)(OAc)_2]$	--do--	9	46
UO_2Br_2	3'-NO_2BAAPS	$[UO_2(3'\text{-}NO_2BAAPS)_2Br_2]$	--do--	10	46
UO_2I_2	3'-NO_2BAAPS	$[UO_2(3'\text{-}NO_2BAAPS)_2I_2]$	--do--	10	46
$UO_2(NCS)_2$	3'-NO_2BAAPS	$[UO_2(3'\text{-}NO_2BAAPS)_2(NCS)_2]$	--do--	10	46
$UO_2(ClO_4)_2$	3'-NO_2BAAPS	$[UO_2(3'\text{-}NO_2BAAPS)_2](ClO_4)_2$	--do--	8	46
$UO_2(NO_3)_2$	3'-NO_2BAAPS	$[UO_2(3'\text{-}NO_2BAAPS)(NO_3)_2]$	--do--	9	46
$UO_2(OAc)_2$	3'-NO_2BAAPS	$[UO_2(3'\text{-}NO_2BAAPS)(OAc)_2]$	--do--	9	46
UO_2Br_2	2'-NO_2BAAPTS	$[UO_2(2'\text{-}NO_2BAAPTS)_2Br_2]$	--do--	10	47
UO_2I_2	2'-NO_2BAAPTS	$[UO_2(2'\text{-}NO_2BAAPTS)_2I_2]$	--do--	10	47
$UO_2(NO_3)_2$	2'-NO_2BAAPTS	$[UO_2(2'\text{-}NO_2BAAPTS)(NO_3)_2]$	--do--	9	47
$UO_2(NCS)_2$	2'-NO_2BAAPTS	$[UO_2(2'\text{-}NO_2BAAPTS)_2(NCS)_2]$	--do--	10	47
$UO_2(OAc)_2$	2'-NO_2BAAPTS	$[UO_2(2'\text{-}NO_2BAAPTS)(OAc)_2]$	--do--	9	47
$UO_2(ClO_4)_2$	2'-NO_2BAAPTS	$[UO_2(2'\text{-}NO_2BAAPTS)_2](ClO_4)_2$	--do--	8	47
UO_2Br_2	3'-NO_2BAAPTS	$[UO_2(3'\text{-}NO_2BAAPTS)_2Br_2]$	--do--	10	47
UO_2I_2	3'-NO_2BAAPTS	$[UO_2(3'\text{-}NO_2BAAPTS)_2I_2]$	--do--	10	47
$UO_2(NO_3)_2$	3'-NO_2BAAPTS	$[UO_2(3'\text{-}NO_2BAAPTS)(NO_3)_2]$	--do--	9	47
$UO_2(NCS)_2$	3'-NO_2BAAPTS	$[UO_2(3'\text{-}NO_2BAAPTS)_2(NCS)_2]$	--do--	10	47
$UO_2(ClO_4)_2$	3'-NO_2BAAPTS	$[UO_2(3'\text{-}NO_2BAAPTS)_2](ClO_4)_2$	--do--	8	47
$UO_2(OAc)_2$	3'-NO_2BAAPTS	$[UO_2(3'\text{-}NO_2BAAPTS)(OAc)_2]$	--do--	9	47
UO_2Br_2	BAAPTS	$[UO_2(BAAPTS)_2Br_2]$	--do--	10	48
UO_2I_2	BAAPTS	$[UO_2(BAAPTS)_2I_2]$	--do--	10	48

$UO_2(NCS)_2$	BAAPTS	$[UO_2(BAAPTS)_2(NCS)_2]$	--do--	10	48
$UO_2(ClO_4)_2$	BAAPTS	$[UO_2(BAAPTS)_2](ClO_4)_2$	--do--	8	48
$UO_2(NO_3)_2$	BAAPTS	$[UO_2(BAAPTS)(NO_3)_2]$	--do--	9	48
$UO_2(OAc)_2$	BAAPTS	$[UO_2(BAAPTS)(OAc)_2]$	--do--	9	48
UO_2Br_2	MBAAPTS	$[UO_2(MBAAPTS)_2Br_2]$	--do--	10	48
UO_2I_2	MBAAPTS	$[UO_2(MBAAPTS)_2I_2]$	--do--	10	48
$UO_2(ClO_4)_2$	MBAAPTS	$[UO_2(MBAAPTS)_2](ClO_4)_2$	--do--	8	48
$UO_2(NO_3)_2$	MBAAPTS	$[UO_2(MBAAPTS)(NO_3)_2]$	--do--	9	48
$UO_2(NCS)_2$	MBAAPTS	$[UO_2(MBAAPTS)_2(NCS)_2]$	--do--	10	48
$UO_2(OAc)_2$	MBAAPTS	$[UO_2(MBAAPTS)(OAc)_2]$	--do--	9	48
UO_2Br_2	HMBAAPTS	$[UO_2(HMBAAPTS)_2Br_2]$	--do--	10	48
UO_2I_2	HMBAAPTS	$[UO_2(HMBAAPTS)_2I_2]$	--do--	10	48
$UO_2(NCS)_2$	HMBAAPTS	$[UO_2(HMBAAPTS)_2(NCS)_2]$	--do--	10	48
$UO_2(ClO_4)_2$	HMBAAPTS	$[UO_2(HMBAAPTS)_2](ClO_4)_2$	--do--	8	48
$UO_2(NO_3)_2$	HMBAAPTS	$[UO_2(HMBAAPTS)(NO_3)_2]$	--do--	9	48
$UO_2(OAc)_2$	HMBAAPTS	$[UO_2(HMBAAPTS)(OAc)_2]$	--do--	9	48
UO_2Br_2	DABAAPTS	$[UO_2(DABAAPTS)_2Br_2]$	--do--	10	49
UO_2I_2	DABAAPTS	$[UO_2(DABAAPTS)_2I_2]$	--do--	10	49
$UO_2(NCS)_2$	DABAAPTS	$[UO_2(DABAAPTS)_2(NCS)_2]$	--do--	10	49
$UO_2(ClO_4)_2$	DABAAPTS	$[UO_2(DABAAPTS)_2](ClO_4)_2$	--do--	8	49
$UO_2(NO_3)_2$	DABAAPTS	$[UO_2(DABAAPTS)(NO_3)_2]$	--do--	9	49
$UO_2(OAc)_2$	DABAAPTS	$[UO_2(DABAAPTS)(OAc)_2]$	--do--	9	49

Infrared studies

The infrared studies reveal that these ligands (Figures 2-12) act as neutral bidentate ligands and the bonding sites are the carbonyl-oxygen and azomethine-nitrogen atom, forming a 5-membered chelate ring. All the ligands have bands around 1650-1640 cm^{-1} [ν(C=O) and 1600-1590 cm^{-1} ν(C=N)]. After complexation the carbonyl frequency appears in the 1605-1570 cm^{-1} region and the azomethine frequency in 1545-1525 cm^{-1} region indicating that these two groups are involved in bonding. In cases of SAAP, HNAAP and HMBAAP the –OH group present does not participate in bonding with uranyl(VI). In far infrared region ν(U-N)/ν(U-O) (metal-ligand bonding) have also been identified. In all the dioxouranium(VI) complexes, the ν_1 and ν_3 modes of O=U=O are assigned in the ranges 835-825 cm^{-1} and 930-925 cm^{-1}, respectively. Wilson's G-F matrix method[53,54] was used to determine the stretching and interaction force constants from which the U-O bond distances were calculated following Badger's formula[55,56]. Depending on the nature of the equatorial ligands the U-O bond distances in dioxouranium(VI) salts generally range from 1.60-1.92 Å[57]. The calculated values of the U-O bond distances in the present complexes are close to 1.73-1.74 Å.

In the case of perchlorato complexes, the strong ν_3 and ν_4 bends in 1105-1080 cm^{-1} and 630-620 cm^{-1} region, respectively, shows the ionic character of the perchlorato group. This view is in conformity with the conductance values and molar mass determination of the complexes studied. For thiocyanato complexes, three fundamental frequencies, *viz.*, ν(C=N), ν(C-S) and δ(NCS) fall in 2050-2030, 830-760 and 465-460 cm^{-1} regions, respectively, suggesting N-bonded NCS in these complexes. The infrared spectra of the nitrato complexes strongly confirm the biocovalent nature of NO_3^- group. Thermal properties of these complexes have been investigated through thermogravimetric (TG) analysis. All the complexes do not show the presence of water molecule either in or out of the coordination sphere. TG

analyses reveal that at *ca*. 630 ºC, U_3O_8 is the final product. In conclusion, the coordination number of uranium(VI) in these complexes is either 8 or 10. The probable structures of these complexes are presented in Figures 13-17.

Uranyl(VI) Complexes of Semicarbazone Derivatives of 4-Aminoantipyrine

Semicarbazones are reported to possess versatile structural features and good antifungal and antibacterial properties[58-63]. We have synthesized and reported a number of 4-aminoantipyrine derived semicarbazones such as 4[N-(benzalidene)amino]antipyrinesemicarbazone (BAAPS), 4[N-(*p*-methoxybenzalidene)amino]-antipyrinesemicarbazone (MBAAPS), 4[N-(2'-nitrobenzalidene)amino]antipyrinesemicarbazone (2'-NO_2BAAPS), 4[N-(3'-nitrobenzalidene)amino]-antipyrinesemicarbazone (3'-NO_2BAAPS), 4[N-(4'-nitrobenzalidene)amino]antipyrinesemicarbazone (4'-NO_2BAAPS), 4[N-(2' hydroxybenzalidene)amino]-antipyrinesemicarbazone (HBAAPS), 4[N-(4'-dimethylaminobenzalidene)amino]-antipyrinesemicarbazone (DABAAPS), 4[N-(4-hydroxy-3-methoxybenzalidene)amino]antipyrinesemicarbazone (HMBAAPS), 4[N-(2-hydroxy-1-naphthalidene)amino]-antipyrinesemicarbazone (HNAAPS), 4[N-(cinnamalidene)amino]antipyrinesemicarbazone (CAAPS), 4[N-(3,4,5 trimethoxybenzalidene)amino]anti-pyrinesemicarbazone (TMBAAPS), 4[N-(furfural)amino]antipyrinesemicarbazone (FFAAPS), 4[N-(4-ethylbenzalidene)amino]antipyrinesemicarbazone (EBAAPS), 4[N-(2,4-dimethylbenzalidene)amino]-antipyrinesemicarbazone (DMBAAPS) and 4[N-(2,4-dichlorobenzalidene)amino]antipyrinesemicarbazone (DCBAAPS). The structures of these semicarbazones are reported in Figures 18-30.

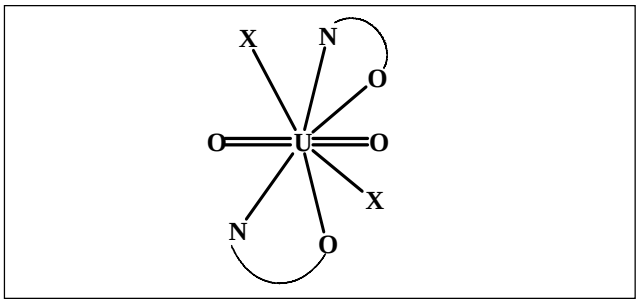

Fig. 13. Structure of $[UO_2(L)_2X_2]$ (X = Cl, Br, I, NCS; L = HNAAP, MBAAP, TMBAAP, DABAAP, HMBAAP, 2'-NO_2BAAP, 3'-NO_2BAAP, CAAP, SAAP or BAAP) (C.N. = 8)

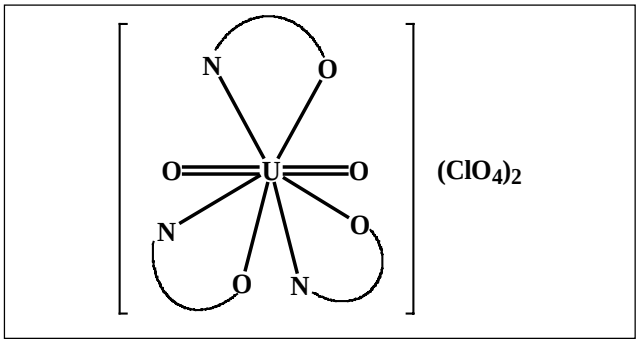

Fig. 14. Structure of $[UO_2(L)_3](ClO_4)_2$ (L = HNAAP, MBAAP, TMBAAP, DABAAP, HMBAAP, 2'-NO_2BAAP, 3'-NO_2BAAP, CAAP, SAAP or BAAP) (C.N. = 8)

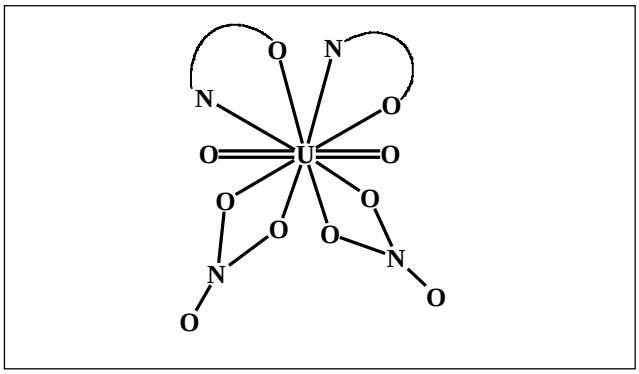

Fig. 15. Structure of $[UO_2(L)_2(NO_3)_2]$ (L = HNAAP, MBAAP, TMBAAP, DABAAP, HMBAAP, 2'-NO_2BAAP, 3'-NO_2BAAP, CAAP, SAAP or BAAP) (C.N. = 10)

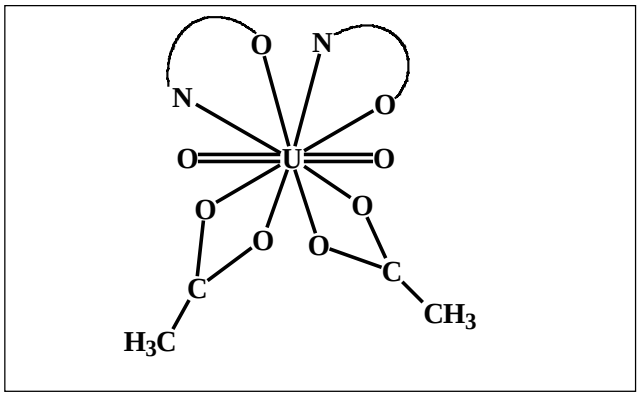

Fig. 16. Structure of $[UO_2(L)_2(OAc)_2]$
(L = HNAAP, MBAAP, TMBAAP, DABAAP, HMBAAP, 2'-NO_2BAAP, 3'-NO_2BAAP, CAAP, SAAP or BAAP)
(C.N. = 10)

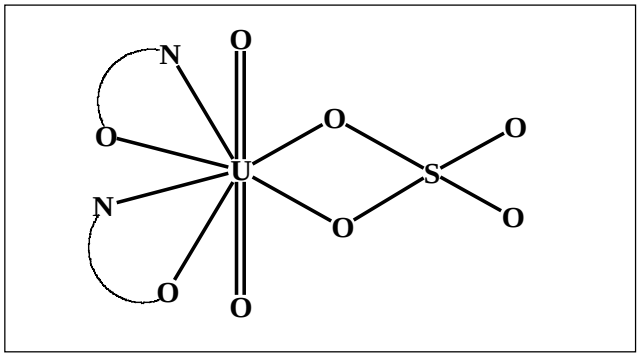

Fig. 17. Structure of $[UO_2(L)_2SO_4]$
(L = BAAP, SAAP, 2'-NO_2BAAP, 3'-NO_2BAAP, DABAAP, MBAAP, HMBAAP, CAAP, HNAAP or FFAAP) (C.N. = 8)

The reaction of dioxouranium(VI) salts with BAAPS, MBAAPS, DABAAPS, 2'-NO_2BAAPS and 3'-NO_2BAAPS forms the complexes with the general composition $UO_2X_2 \cdot nL$ (X = Br, I, NCS or ClO_4, n = 2; X = NO_3 or OAc, n = 1, L = BAAPS, MBAAPS, DABAAPS, 2'-NO_2BAAPS or 3'-NO_2BAAPS)[45,46] (Table 1). All these complexes are anhydrous, which is evident from the analytical, infrared spectral and thermogravimetric studies. Among the UO_2(VI)-semicarbazone complexes containing bromo, iodo, thiocyanato, nitrato or acetato ligands are non-electrolytes in nature in $PhNO_2$. However, the perchlorato UO_2(VI)-semicarbazone complexes behave as 1:2 electrolytes in $PhNO_2$.

Infrared studies

The infrared studies reveal that these semicarbazones act as a neutral tridentate (N,N,O) coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms. The oxouranium O=U=O absorption bands ν_1 and ν_3 were also identified. In far infrared regions ν(U-N)/ν(U-O) have also been identified in these complexes. In all the thiocyanato complexes, the NCS^- coordinates through N-atom while NO_3^- is bicovalently bonded. However, perchlorato ions in these complexes do not take part in coordination and remain outside the coordination sphere.

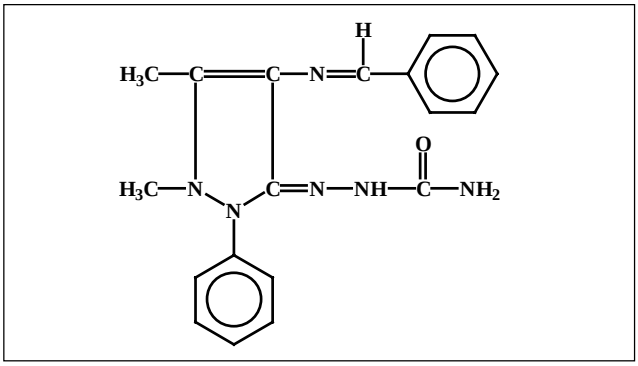

Fig. 18. Structure of 4[N-(benzalidene)-amino]antipyrinesemicarbazone (BAAPS)

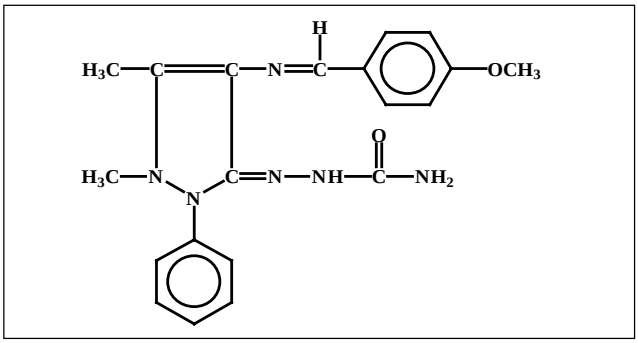

Fig. 19. Structure of 4[N-(4'-methoxy-benzalidene)amino]antipyrinesemicarbazone (MBAAPS)

Thermal properties of these complexes have also been investigated. The proposed structures of these compounds are presented in Figures 31-34. Depending on the nature of anion present, the coordination number of U(VI) in these coordination compounds are either 8, 9 or 10.

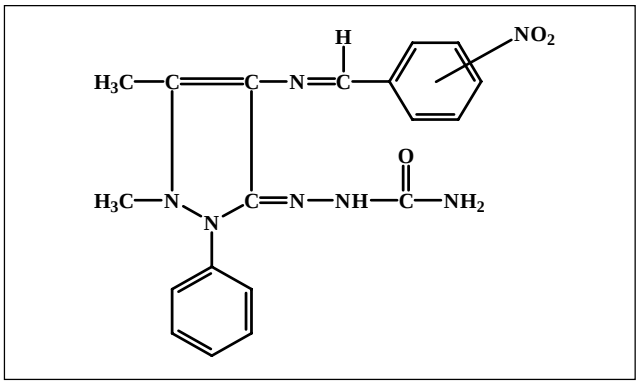

Fig. 20. Structure of 4[N-(2'-nitrobenzalidene)amino]-antipyrinesemicarbazone (2'-NO_2BAAPS); (3'-NO_2BAAPS); (4'-NO_2BAAPS)

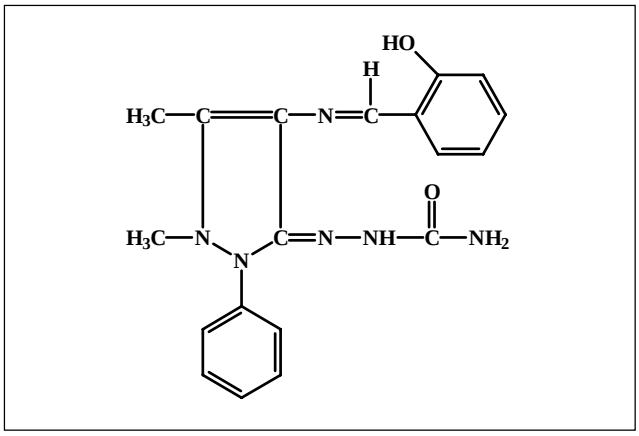

Fig. 21. Structure of 4[N-(2'-hydroxybenzalidene)-amino]antipyrinesemicarbazone (HBAAPS)

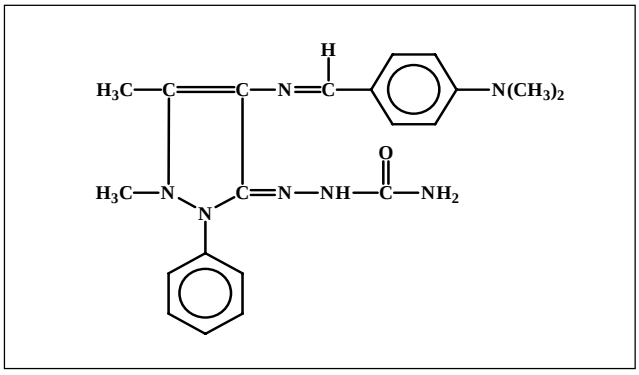

Fig. 22. Structure of 4[N-(4'-dimethyl-aminobenzalidene)amino]antipyrinesemicarbazone (DABAAPS)

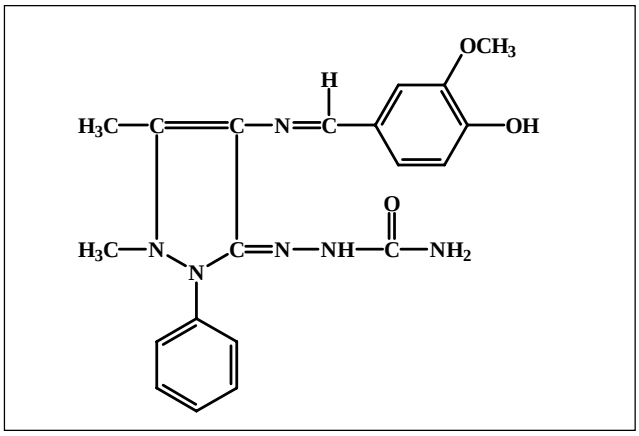

Fig. 23. Structure of 4[N-(4'-hydroxy-3'-methoxybenzalidene)amino]antipyrinesemicarbazone (HMBAAPS)

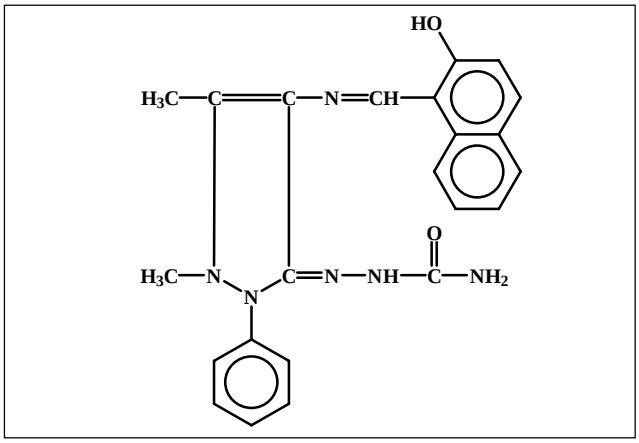

Fig. 24. Structure of 4[N-(2'-hydroxy-1'-naphthalidene)-amino]antipyrinesemicarbazone (HNAAPS)

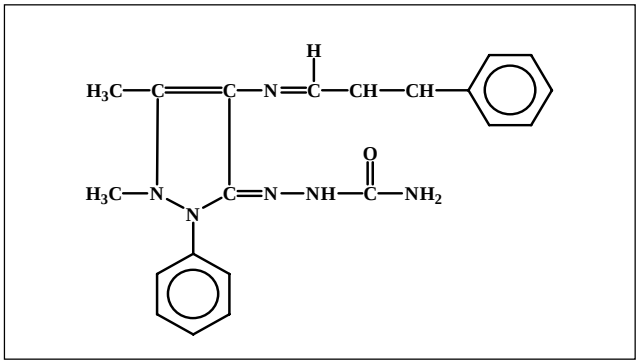

Fig. 25. Structure of 4[N-(cinnamalidene)-amino]antipyrinesemicarbazone (CAAPS)

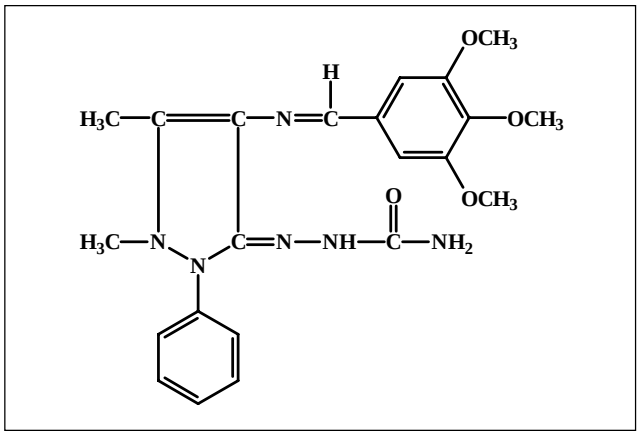

Fig. 26. Structure of 4[N-(3',4',5'-trimethoxybenzalidene)amino]antipyrinesemicarbazone (TMBAAPS)

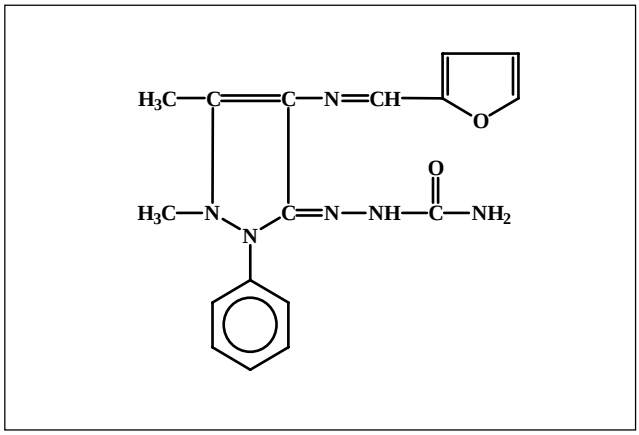

Fig. 27. Structure of 4[N-(furfural)amino]antipyrine-semicarbazone (FFAAPS)

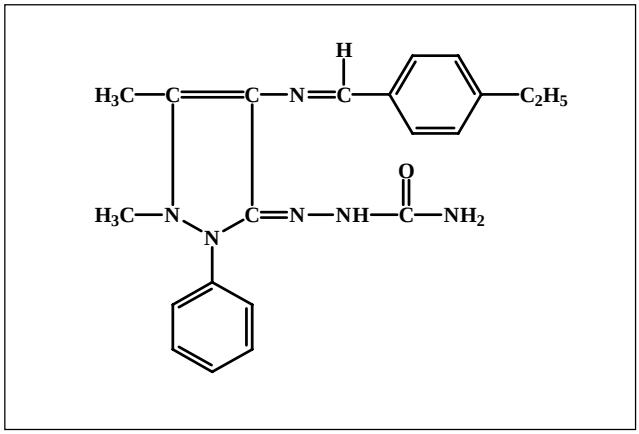

Fig. 28. Structure of 4[N-(4'-ethylbenzalidene)amino]antipyrinesemicarbazone (EBAAPS)

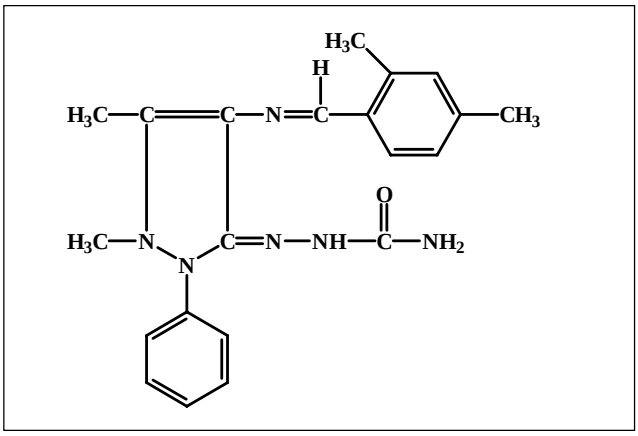

Fig. 29. Structure of 4[N-(2',4'-dimethylbenzalidene)-amino]antipyrinesemicarbazone (DMBAAPS)

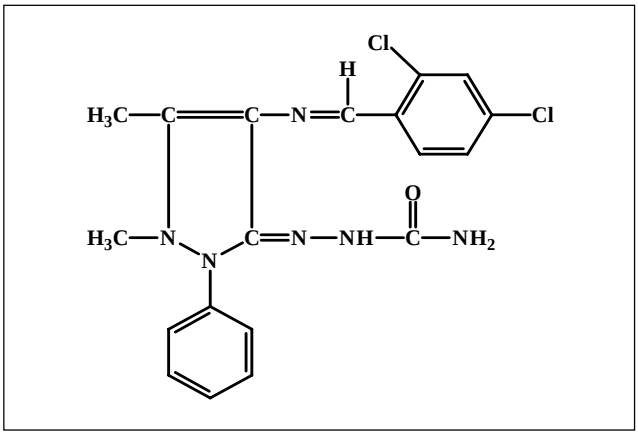

Fig. 30. Structure of 4[N-(2',4'-dichlorobenzalidene)amino]antipyrinesemicarbazone (DCBAAPS)

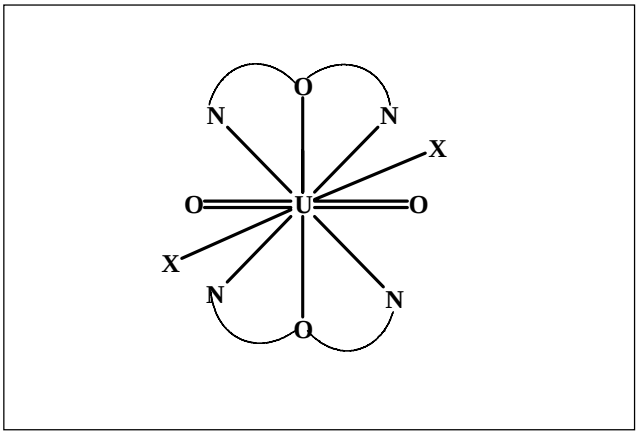

Fig. 31. Structure of $[UO_2(L)_2X_2]$ (X = Br, I, NCS; L = BAAPS, MBAAPS, DABAAPS, 2'-NO_2BAAPS or 3'-NO_2BAAPS) (C.N. = 10)

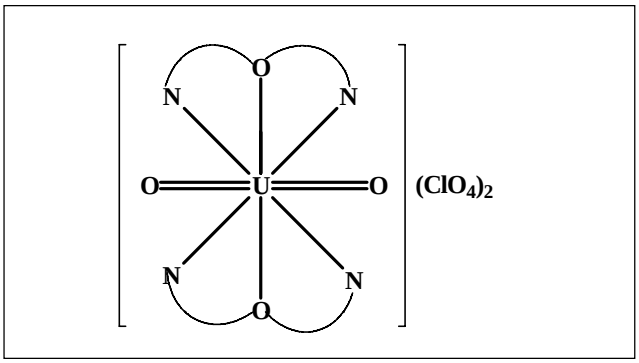

Fig. 32. Structure of $[UO_2(L)_2](ClO_4)_2$ (L = BAAPS, MBAAPS, DABAAPS, 2'-NO_2BAAPS or 3'-NO_2BAAPS) (C.N. = 8)

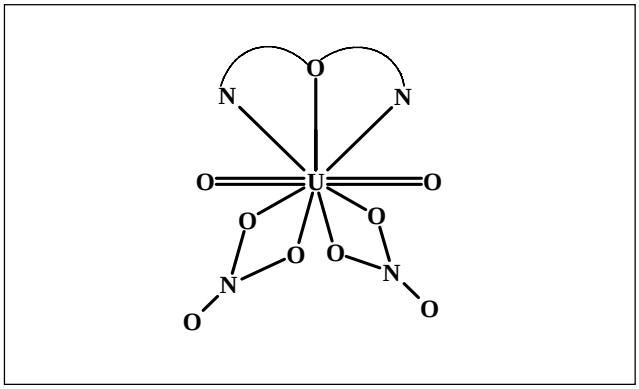

Fig. 33. Structure of $[UO_2(L)(NO_3)_2]$ (L = BAAPS, MBAAPS, 2'-NO_2BAAPS or 3'-NO_2BAAPS) (C.N. = 9)

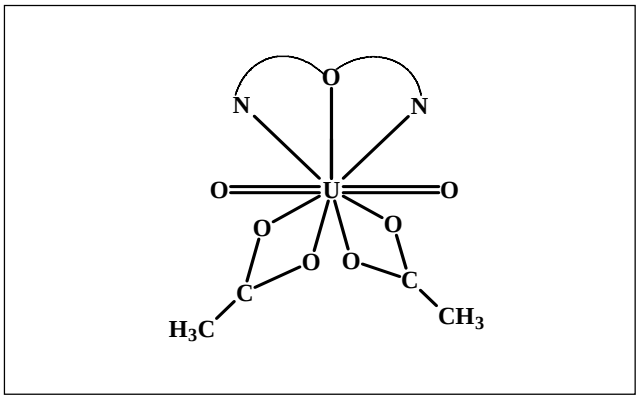

Fig. 34. Structure of $[UO_2(L)(OAc)_2]$ (L = BAAPS, MBAAPS, 2'-NO_2BAAPS or 3'-NO_2BAAPS) (C.N. = 9)

Uranyl(VI) Complexes of Thiosemicarbazone Derivatives of 4-Aminoantipyrine

During the last two decades, thiosemicarbazones derived from 4-aminoantipyrine have emerged as an important class of sulfur donor ligands for transition metal ions[47-49,64-66]. The interest to develop the coordination chemistry of thiosemicarbazones is because of their biological and medicinal properties. They present a variety of biological activities ranging from antitumor, fungicide, bactericide, anti-inflammatory and antiviral activities. However, little is known about the dioxouranium(VI) complexes of thiosemicarbazones of 4-aminoantipyrine. In our laboratory, we have synthesized 4[N-(benzalidene)-amino]antipyrinethiosemicarbazone (BAAPTS), 4[N-(2'-nitrobenzalidene)amino]antipyrinethiosemicarbazone (2'-NO_2BAAPTS), 4[N-(3'-nitrobenzalidene)-amino]antipyrinethiosemicarbazone (3'NO_2BAAPTS), 4[N-(4'-methoxybenzalidene)amino]antipyrinethio-semicarbazone (MBAAPTS), 4[N-(4-hydroxy-3-methoxybenzalidene)amino]antipyrinethio-semicarbazone (HMBAAPTS), 4[N-(4-dimethylaminobenzalidene)amino]antipyrinethio-semicarbazone (DABAAPTS). The structure of these ligands are shown in Figures 35-40[47-49].

The reaction of dioxouranium(VI) salts with BAAPTS, 2'-NO_2BAAPTS, 3'-NO_2BAAPTS, MBAAPTS, HMBAAPTS and DABAAPTS resulted in the formation of the complexes with the general composition $UO_2X_2 \cdot nL$ (X = Br, I, NCS or ClO_4, n = 2; X = NO_3 or OAc, n = 1, L = BAAPTS, 2'-NO_2BAAPTS, 3'-NO_2BAAPTS, MBAAPTS, HMBAAPTS or DABAAPTS[47-49] and are shown in Table1. All these thiosemicarbazones ligands behave as neutral tridentate (N,N,S) ligands. The proposed structures of these compounds are presented in Figures 41-44. The coordination number of U(VI) in these complexes are either 8, 9 or 10 which depends on the nature of anion present.

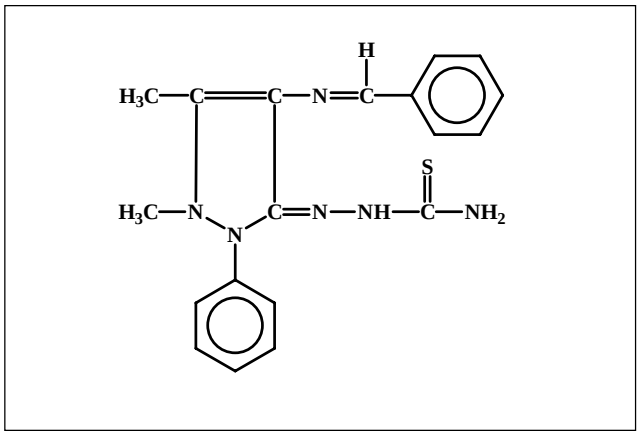

Fig. 35. Structure of 4[N-(benzalidene)-amino]antipyrinethiosemicarbazone (BAAPTS)

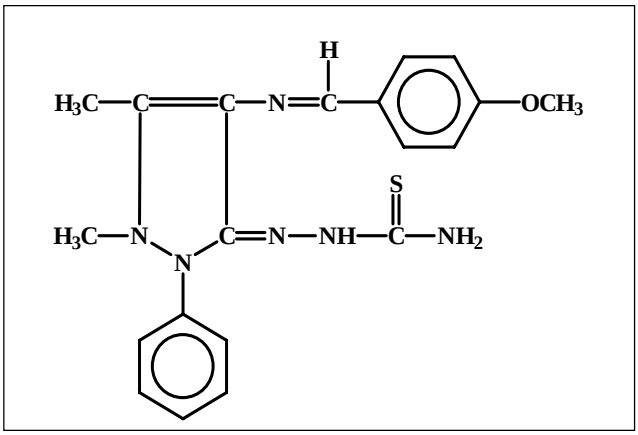

Fig. 38. Structure of 4[N-(4'-methoxybenzalidene)-amino]antipyrinethiosemicarbazone (MBAAPTS)

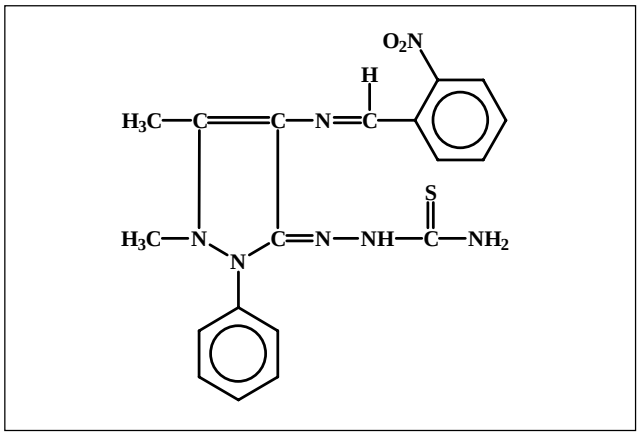

Fig. 36. Structure of 4[N-(2'-nitrobenzalidene)amino]-antipyrinethiosemicarbazone (2'-NO_2BAAPTS)

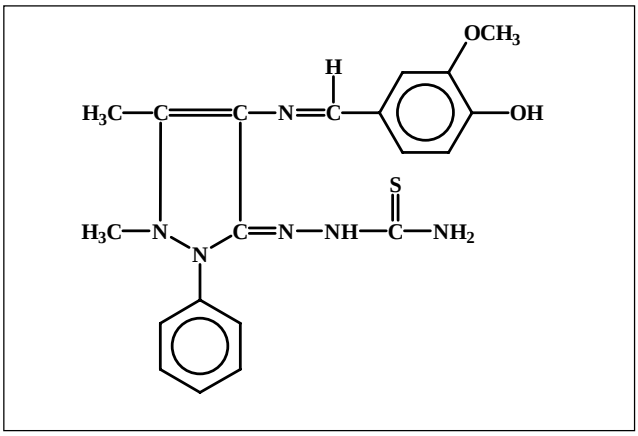

Fig. 39. Structure of 4[N-(4'-hydroxy-3'-methoxybenzalidene)amino]antipyrinethiosemicarbazone (HMBAAPTS)

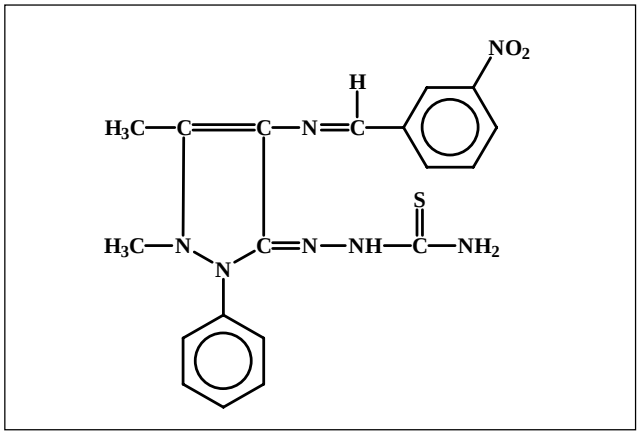

Fig. 37. Structure of 4[N-(3'-nitrobenzalidene)amino]-antipyrinethiosemicarbazone (3'-NO_2BAAPTS)

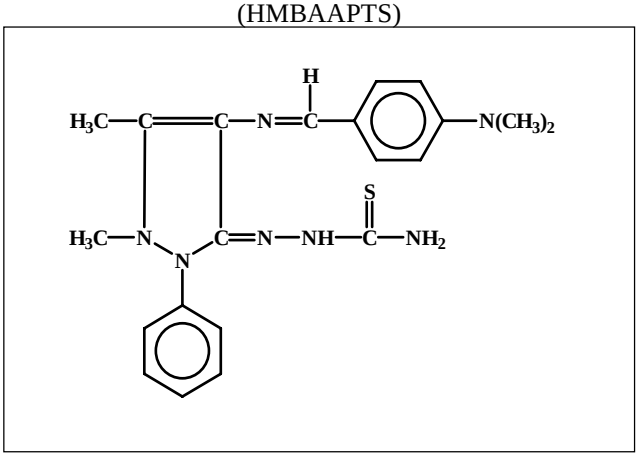

Fig. 40. Structure of 4[N-(4'-dimethylaminobenzalidene)-amino]antipyrinethiosemicarbazone (DABAAPTS)

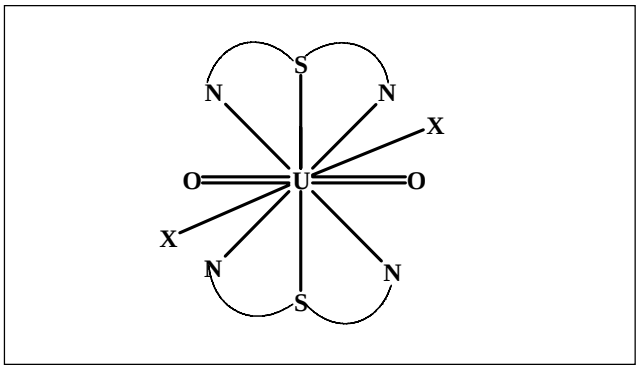

Fig. 41. Structure of $[UO_2(L)_2X_2]$ (X = Cl, Br or NCS; L = 2'-NO_2BAAPTS, 3'-NO_2BAAPTS, BAAPTS, MBAAPTS, HMBAAPTS or DABAAPTS) (C.N. = 10)

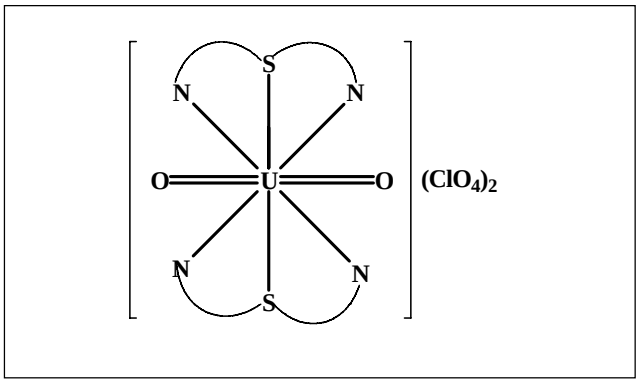

Fig. 42. Structure of $[UO_2(L)_2](ClO_4)_2$ (L = 2'-NO_2BAAPTS, 3'-NO_2BAAPTS, BAAPTS, MBAAPTS, HMBAAPTS or DABAAPTS) (C.N. = 8)

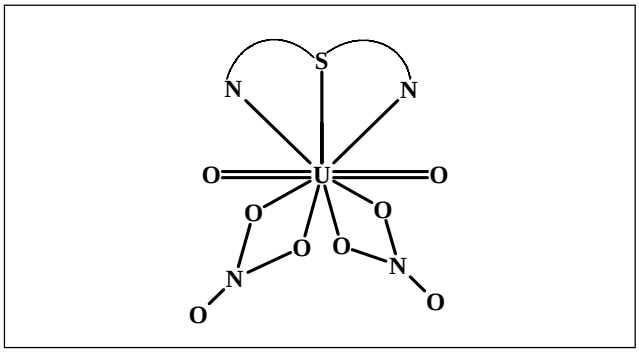

Fig. 43. Structure of $[UO_2(L)(NO_3)_2]$ (L = 2'-NO_2BAAPTS, 3'-NO_2BAAPTS, BAAPTS, MBAAPTS, HMBAAPTS or DABAAPTS) (C.N. = 9)

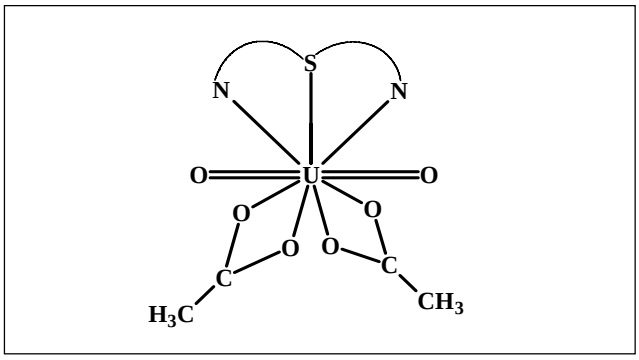

Fig. 44. Structure of $[UO_2(L)(OAc)_2]$ (L = 2'-NO_2BAAPTS, 3'-NO_2BAAPTS, BAAPTS, MBAAPTS, HMBAAPTS or DABAAPTS) (C.N. = 9)

Some Examples of Mixed Ligand Complexes of UO_2(VI)-Semicarbazones as Primary Ligand and Sulphoxide as Secondary Ligand

In literature, coordination number of upto 14 has been reported for uranium(VI)[10]. With interest to enhance the coordination number, we attempted to synthesize some mixed ligand complexes of UO_2^{2+} in which semicarbazones as primary ligand and sulphoxides as secondary ligand and are reported in Table 2. A good number of mixed ligand complexes with the general composition $UO_2(L)_n(DMSO)X_2$ (X = Br, I, NCS, NO_3, OAc, n = 1, X = ClO_4, L = FFAAPS or CAAP); $[UO_2(L)(DPSO)(OAc)_2]$ (L = BAAPS, HBAAPS, MBAAPS, DABAAPS, 2'-NO_2BAAPS, 3'-NO_2BAAPS, 4'-NO_2BAAPS, HMBAAPS, HNAAPS, CAAPS, TMBAAPS, FFAAPS); $[UO_2(L)(TMSO)SO_4]$ (L = BAAPS, HBAAPS, MBAAPS, 2'-NO_2BAAPS, 3'-NO_2BAAPS, 4'-NO_2BAAPS, DABAAPS, HMBAAPS, HNAAPS, CAAPS, TMBAAPS, FFAAPS, EBAAPS, DMBAAPS or DCBAAPS) were synthesized. Infrared studies and other analytical studies on these complexes reveal that the semicarbazones are neutral tridentate (N,N,O) and DMSO, DPSO or TMSO is coordinated *via* their lone oxygen atom. The coordination number of U(VI) in these coordination compounds are either 8, 9 or 10[50-52]. We have been unsuccessful in the attempt to isolate complexes of U(VI) with coordination number more than 10. The structures of these complexes are shown in Figures 45-50.

Conclusions

This review summarizes the progress in uranyl(VI) complexes of Schiff bases derived from 4-aminoantipyrine, semicarbazone and thiosemicarbazone derivatives of 4-aminoantipyrine and some mixed ligand complexes of uranyl(VI)-semicarbazones as primary ligand and sulphoxide as secondary ligand. The reported complexes have been synthesized in our laboratory. A continuing trend in uranyl(VI) complexes of Schiff bases research has been observed which is a strong emphasis on applications of such complexes in various fields.

Table 2. Mixed ligand complexes of dioxouranium(VI) derived from semicarbazones and sulphoxides.

Lewis acid	Ligand	Composition of the complexes	Physico-chemical studies	Coord. no.	Refe-rence
UO_2Br_2	FFAAPS & DMSO	$[UO_2(FFAAPS)(DMSO)Br_2]$	Elemental analysis, molar conductance, molar mass, infrared, thermogravimetric analysis and XRD	8	50
UO_2I_2	FFAAPS & DMSO	$[UO_2(FFAAPS)(DMSO)I_2]$	--do--	8	50
$UO_2(NCS)_2$	FFAAPS & DMSO	$[UO_2(FFAAPS)(DMSO)(NCS)_2]$	--do--	8	50
$UO_2(NO_3)_2$	FFAAPS & DMSO	$[UO_2(FFAAPS)(DMSO)(NO_3)_2]$	--do--	10	50
$UO_2(OAc)_2$	FFAAPS & DMSO	$[UO_2(FFAAPS)(DMSO)(OAc)_2]$	--do--	10	50
$UO_2(ClO_4)_2$	FFAAPS & DMSO	$[UO_2(FFAAPS)(DMSO)](ClO_4)_2$	--do--	9	50
UO_2Br_2	CAAPS & DMSO	$[UO_2(CAAPS)(DMSO)Br_2]$	--do--	8	50
UO_2I_2	CAAPS & DMSO	$[UO_2(CAAPS)(DMSO)I_2]$	--do--	8	50
$UO_2(NCS)_2$	CAAPS & DMSO	$[UO_2(CAAPS)(DMSO)(NCS)_2]$	--do--	8	50
$UO_2(NO_3)_2$	CAAPS & DMSO	$[UO_2(CAAPS)(DMSO)(NO_3)_2]$	--do--	10	50
$UO_2(OAc)_2$	CAAPS & DMSO	$[UO_2(CAAPS)(DMSO)(OAc)_2]$	--do--	10	50
$UO_2(ClO_4)_2$	CAAPS & DMSO	$[UO_2(CAAPS)(DMSO)](ClO_4)_2$	--do--	9	50
$UO_2(OAc)_2$	BAAPS & DPSO	$[UO_2(BAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	HBAAPS & DPSO	$[UO_2(HBAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	MBAAPS & DPSO	$[UO_2(MBAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	DABAAPS & DPSO	$[UO_2(DABAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	2'-NO_2BAAPS & DPSO	$[UO_2(2'$-$NO_2BAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	3'-NO_2BAAPS & DPSO	$[UO_2(3'$-$NO_2BAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	4'-NO_2BAAPS & DPSO	$[UO_2(4'$-$NO_2BAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	HMBAAPS & DPSO	$[UO_2(HMBAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	HNAAPS & DPSO	$[UO_2(HNAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	CAAPS & DPSO	$[UO_2(CAAPS)(DPSO)(OAc)_2]$	--do--	10	51
$UO_2(OAc)_2$	TMBAAPS & DPSO	$[UO_2(TMBAAPS)(DPSO)(OAc)_2]$	--do--	10	51

$UO_2(OAc)_2$	FFAAPS & DPSO	$[UO_2(FFAAPS)(DPSO)(OAc)_2]$	--do--	10	51
UO_2SO_4	BAAPS & TMSO	$[UO_2(BAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	HBAAPS & TMSO	$[UO_2(HBAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	MBAAPS & TMSO	$[UO_2(MBAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	2'-NO_2BAAPS & TMSO	$[UO_2(2'\text{-}NO_2BAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	3'-NO_2BAAPS & TMSO	$[UO_2(3'\text{-}NO_2BAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	4'-NO_2BAAPS & TMSO	$[UO_2(4'\text{-}NO_2BAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	DABAAPS & TMSO	$[UO_2(DABAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	HMBAAPS & TMSO	$[UO_2(HMBAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	HNAAPS & TMSO	$[UO_2(HNAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	CAAPS & TMSO	$[UO_2(CAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	TMBAAPS & TMSO	$[UO_2(TMBAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	FFAAPS & TMSO	$[UO_2(FFAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	EBAAPS & TMSO	$[UO_2(EBAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	DMBAAPS & TMSO	$[UO_2(DMBAAPS)(TMSO)SO_4]$	--do--	8	52
UO_2SO_4	DCBAAPS & TMSO	$[UO_2(DCBAAPS)(TMSO)SO_4]$	--do--	8	52

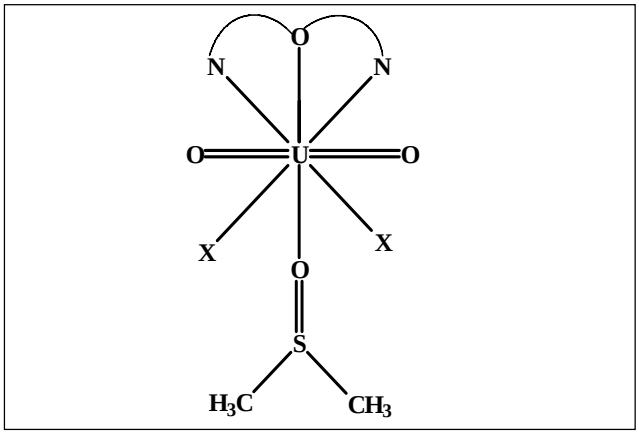

Fig. 45. Structure of $[UO_2(L)\cdot DMSO\cdot X_2]$ (X = Br, I or NCS; L = FFAAPS or CAAPS) (C.N. = 8)

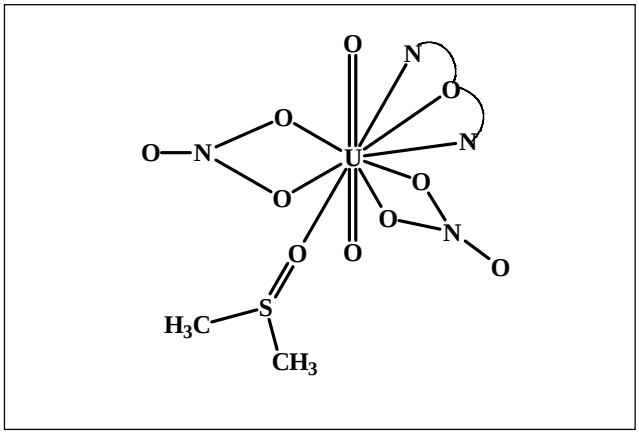

Fig. 46. Structure of $[UO_2(L)\cdot DMSO\cdot(NO_3)_2]$ (L = FFAAPS or CAAPS) (C.N. = 10)

Acknowledgement

The authors are thankful to the University Research Committee of the University of the South Pacific, Suva, Fiji for financial support in form of a project grant No. 6394-1321 and 6395-1321.

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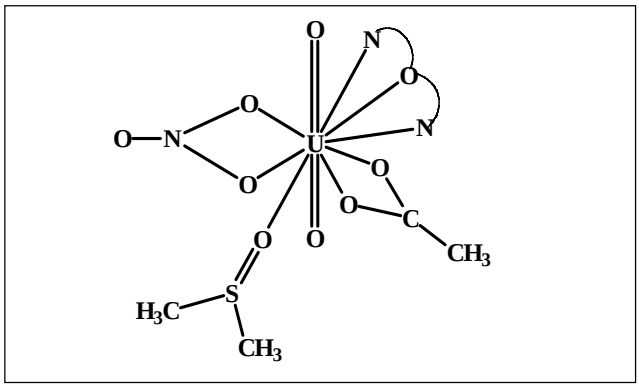

Fig. 47. Structure of $[UO_2(L)\cdot DMSO(OAc)_2]$ (L = FFAAPS or CAAPS) (C.N. = 10)

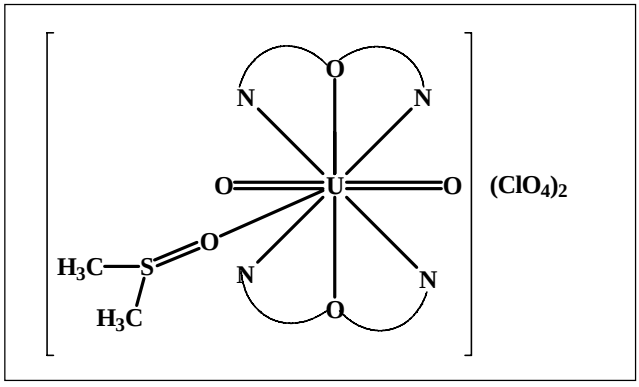

Fig. 48. Structure of $[UO_2(L)_2\cdot DMSO](ClO_4)_2$ (L = FFAAPS or CAAPS) (C.N. = 10)

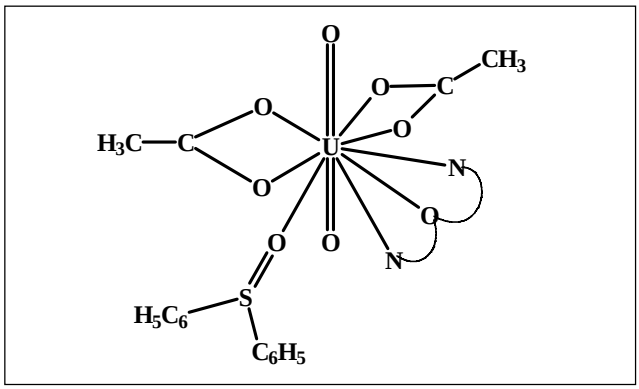

Fig. 49. Structure of $[UO_2(L)(DPSO)(OAc)_2]$ (L = BAAPS, HBAAPS, MBAAPS, DABAAPS, 2'-NO_2BAAPS, 3'-NO_2BAAPS, 4'-NO_2BAAPS, HMBAAPS, HNAAPS, CAAPS, TMBAAPS or FFAAPS) (C.N. = 10)

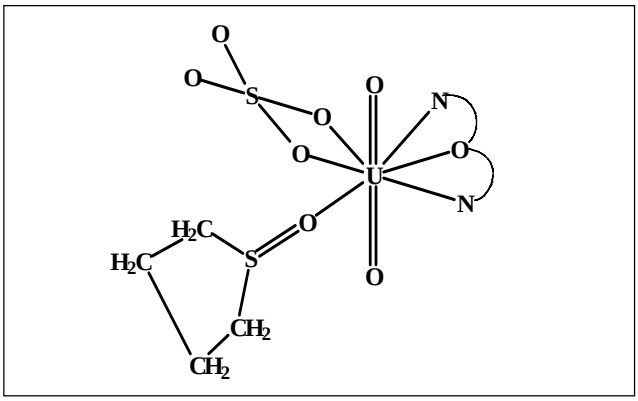

Fig. 50. Structure of $[UO_2(L)SO_4\cdot TMSO]$ (L = BAAPS, HBAAPS, MBAAPS, 2'-, 3'-, 4'-NO_2BAAPS, DABAAPS, HMBAAPS, HNAAPS, CAAPS, TMBAAPS, FFAAPS, EBAAPS, DMBAAPS or DCBAAPS) (C.N. = 8)

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MS Received September 11, 2012, Accepted September 30, 2012