MIXED LIGAND COMPLEXES OF URANIUM (VI) WITH ACETONE NICOTINOYL AND ISONICOTINOYL HYDRAZONES

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Abstract: Acetone nicotinoylhydrazone (ANH) and acetone isonicotinoylhydrazone (AINH) and their mixed ligand complexes with dioxouranium; $[UO_2(ANH)_2(NO_3)_2]$ xH_2O (1), $[UO_2(AINH)_2(NO_3)_2]$ xH_2O (2), $[UO_2(ANH)_2(CH_3COO)_2]xH_2O$ (3) and $[UO_2(AINH)_2(CH_3COO)_2]xH_2O$ (4) were synthesized. The compounds were characterized by melting point, solubility, conductivity measurement, infrared, elemental analysis and electronic spectral studies. The Schiff's base ligands act as bidentate donors using the carbonyl O and the azomethine N as binding sites to form stable metal chelates. The complexes adopt octahedral geometry with two ligands coordinated to the metal ion, while the fifth and sixth positions are occupied by NO_3^- for the nitrate complexes and CH_3COO^- for the acetato complexes. The acetate and nitrate coligands were found to coordinate via unidentate mode. The compounds have moderate melting points and are nonelectrolytes in solution, relatively stable and insoluble in common solvents except in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). Electronic spectra revealed that the complexes exhibited intraligand and charge transfer transitions accounting for the complexes' yellow colour. The NO_3^- containing complexes 1 and 3 exhibited slight inhibition of the growth of Gram-positive *S. aureus* showing improvement over the inactive ANH ligand. The recognition ability of the ligands for the uranium ion and the stability of the complexes formed make the ligands good candidate species in the metal ion pollution remediation and in its spectroscopic determination.

Keywords: Hydrazone, nicotinoylhydrazone, acetone isonicotinoylhydrazone, Schiff base, antimicrobial

Introduction

Hydrazones belong to the class of asymmetric Schiff base (El-Saied *et al.*, 2011; Chowdhury *et al.*, 2008). Hydrazones and similar organic compounds have continued to attract profound attention due to their biological, physiological and therapeutic actions (Popiolek and Biernasiuk, 2017; Khattab *et al*, 2016; Han *et al.,* 2017; Govindasami, 2011; Nwabueze, 1996; Hermes-Lima *et al.*, 2001) and such activities are improved upon coordination to metal ion (Banerjee *et al,* 2019; Bekheit *et al* 2013; Zaky *et al.*, 2012). This is because metal ions generally are tuneable species whose redox potentials can be easily altered by the electronic nature and/or structure of the ligands (Grochala *et al.*, 2001). Because hydrazones can bind metal reversibly make them candidates of choice as Dynamic Combinatorial Library (DCL) in the new dynamic combinatorial chemistry. This research area has brought about the screening of several low and medium molecular weight hydrazones DCL which is yielding encouraging results in drug discovery (Williams and Lehn, 2004; Regis and Ivan, 2003; Bunyapaiboonsri, 2001; Ivan and Lehn, 1997).

Similarly, interest in the investigation of actinide amido complexes as well defined precursor materials for synthetic chemistry lies in their rich reaction chemistry, including alteration of molecular nitrogen (Oldham *et al.*, 2002). Uranium has also witnessed increased industrial activity, such that interest in the study of uranium and its compounds is also focusing environmental management of this element since uranium mining and dump sites poses a great danger to the environment. Therefore, waste and mining site remediation and stewardship of uranium is required. Of particular concern is the fate of uranium complexed with organic and inorganic compounds at the waste site (Merroun *et al.*, 2000).

Whether for effective synthesis of uranium complexes as precursor materials and/or effective remediation on the one hand and having good knowledge of the nature and interaction/association of the hydrazones ligand for exploiting its application in DCL and indeed supramolecular assemblies on the other hand, a detailed understanding of the structural and physical properties of uranium complexes with the Schiff's base is required. Here, we report the synthesis and characterization of complexes of acetone nicotinoyl and the isonicotinoyl hydrazones analogue with uranyl ion.

Materials and Methods

Experimental

Reagent and solvents

Ethylnicotinate and ethylisonicotinate were Sigma-Aldrich reagents while uranylnitrate and uranylacetate were from BDH. All other chemicals used were of AR grade and were used without further purification

Instrumental measurement

Infrared spectra were recorded as nujol disc on a Mattson Genesis II FTIR spectrophotometer and the electronic spectra were taken on a Beckman Du530 Uv-visible Spectrophotometer. The conductivity and melting point/decomposition temperature measurements were made on Jenway 4330 conductivity and pH meter and an IA900 series electrothermal melting point apparatus, respectively.

Elemental analysis

Uranium (as oxine complex) was determined gravimetrically by standard method (Jeffery *et al.*, 1978).

Preparations

Preparation of acetone nicotinoyl hydrazone

Nicotinic acid hydrazide was prepared from ethylnicotinate and hydrazine monohydrate according to method described in literature (Ikekwere *et al.*, 1989).

The acetone nicotinoylhydrazone (ANH) was prepared by adding 7.74 g (0.056 moles) of nicotinic acid hydrazide to 4.08 mL (3.28 g 0.056 moles) of acetone in 40 ml absolute ethanol in a round bottom flask. The mixture was refluxed for about four hours. The product was collected in a beaker and left to crystallized. The solid was recrystallized from ethanol and dried over calcium chloride in vacuum desiccators and then weighed (Yield 42.60%).

Acetone isonicotinoylhydrazone (AINH) was prepared in a similar way (Yield 59.38%).

Preparation of the complexes

$[UO_2(ANH)_2(NO_3)_2]$ xH_2O (1)

The complex was prepared by dissolving 5.02 g (0.1 moles) of uranylnitrate in 100 mL distilled water, and added drop wise

with magnetic stirring to a 100 mL ethanolic solution of 1.5g (0.1 moles) of acetone nicotinoylhydrazone. Stirring was continued for a further 10 min and left standing for one hour. The yellow crystals were removed by filtration, washed with cold water and dried over calcium chloride in vacuum desiccators.

[UO₂(AINH)₂(NO₃)₂] *x*H₂O (**2**), was prepared following the same route.

[UO₂(ANH)₂(CH₃COO)₂]xH₂O(3) and
[UO₂(AINH)₂(CH₃COO)₂]xH₂O (4)

The same synthesis procedure was repeated using 4.24 g (0.1 moles) uranylacetate and 1.5 g (0.1 moles) of **ANH** and **AINH,** respectively.

Antimicrobial studies

The screening of the hydrazones and the complexes were carried out in nutrient agar medium. They were examined against two Gram-negative bacteria; *P. aeruginosa* and *E. coli*, a Gram-positive *S. aureus* and one fungi *C. albican.* The

petridishes for the work were impregnated with disks containing the solutions of the test samples and air dried for 4 h. The isolates for evaluation were then incubated on a plate. This was done by striking uniformly with sterile wire loop after which the disks at 2 cm spacing were applied to the surface of the plate. This was done in duplicate. Antibacterial action was measured as zone diameter of inhibition around the disk.

Results and Discussion

Brown coloured hydrazonescrystals were obtained via the reaction Scheme 1. The yield and other physiochemical properties are shown in Table 1.
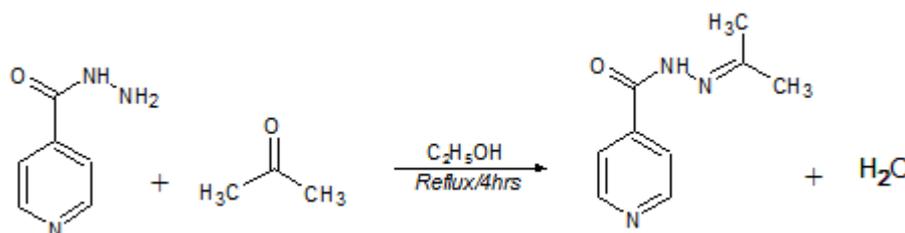
Scheme 1: Route to the synthesis of acetone nicotinoylhydrazone (ANH)

The acetone isonicotinoylhydrazones (AINH) follow similar route.

The metal analysis reveal that the coordination of the hydrazone moieties to the UO_2^{2+} in the nitrate and acetate salt solutions form a 1:2 M:L chelates with respect to the hydrazone ligands, this is illustrated in equations 1 and 2;

$RCONHNC(CH_3)_2 + UO_2(NO_3)_2.6H_2O \rightarrow [UO_2(RCONHNC(CH_3)_2)_2(NO_3)_2].xH_2O$
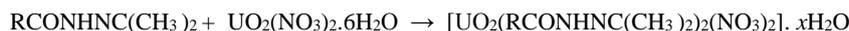
for complexes (**1**) and (**2**)   (eqn 1)

$RCONHNC(CH_3)_2 + UO_2(CH_3COO)_2.2H_2O \rightarrow [UO_2(RCONHNC(CH_3)_2)_2(CH_3COO)_2].xH_2O$

for complex (**3**) and (**4**)   (eqn 2)

Table 1: some Physical Constant for the ligands and complexes

Compound	Formula	Formula weight	Colour	M.Pt/Dec Temp ºC	%Yield	%M	Conductivity cm⁻²mol⁻¹
ANH	C₉H₁₁N₃O	117	Brown	175	42.60	-	0.00
AINH	C₉H₁₁N₃O	117	Brown	177	59.30	-	0.00
1	C₁₈H₂₂N₈O₈U	716	yellow	153	45.00	31.93 (33.22)	0.11
2	C₁₈H₂₂N₈O₈U	716	yellow	158	27.40	31.00 (33.22)	0.10
3	C₂₄H₃₆N₆O₆U	742	yellow	174	32.40	30.55 (32.05)	0.06
4	C₂₂H₂₈N₆O₉U	742	yellow	164	25.40	32.46 (32.05)	0.01

The ligands were sufficiently soluble in ethanol and other common organic solvents, they were however insoluble in water. The complexes were insoluble in most organic solvents tested, but soluble in DMSO and DMF. They all displayednonelectrolytic character in solution with moderate melting points indicating they are non-ionic in nature.

Infrared spectra

The IR bands at 3320 and 3300 cm⁻¹ in the spectra of ANH and AINH respectively is assigned to hydrogen bonded hydroxyl group stretching vibrations, suggesting that the ligands are hydrogen bonded via OH group. The possible modes of OH hydrogen bonding in the molecules are presented in Scheme 2. The intensities and positions of the hydrogen bonded OH bands in the ligands changed drastically

in the complexes. The absences of typical band around 3550-3450 cm⁻¹ in the spectral of the ligands suggest non-dimeric OH stretching which rule out form II. The ligands are most likely H-bonded as shown in form I in Scheme 2.

The mode of coordination of the ligand to the metal ion was thus examined by a comparison of the IR spectra to those of the free ligands. The appearances of strong band at 938-912 cm⁻¹ in the spectral of complexes which is associated with ν [O=U=O] modes of IR vibration is consistent with the coordination of the UO_2^{2+} centre to the hydrazone ligands (Sule, 2009; Nakamoto, 1997a).

The bands in the free ligand spectra at 1666 and 1642 cm⁻¹ is assigned to ν [C=O] and those at *ca* 3260 and 3300 cm⁻¹ to

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[N-H] vibrations. The bands appearing at these regions are all drastically weakened and shifted in the complexes to lower frequency and band broadening occur in this region in complex 4 displaying only one unresolved band at around 3300 cm⁻¹. This shift is very characteristic of several hydrazones ligands coordinated through the azomethine nitrogen atom and the carbonyl oxygen. Of significance in this mode of coordination is the comparison of the [C=N] mode displayed in the free ligand at *ca* 1580 cm⁻¹ compared to those

of the complex spectra at around 1540 cm⁻¹ showing a shift to higher wave number further indicating the involvement of the nitrogen atom of the C=N specie in coordination. From the IR spectra analysis it is thus instructive that both the azomethine N and the O atom of the carbonyl group of the ligand coordinate to the metal ion thereby forming a metal chelate as illustrated in Scheme 3.
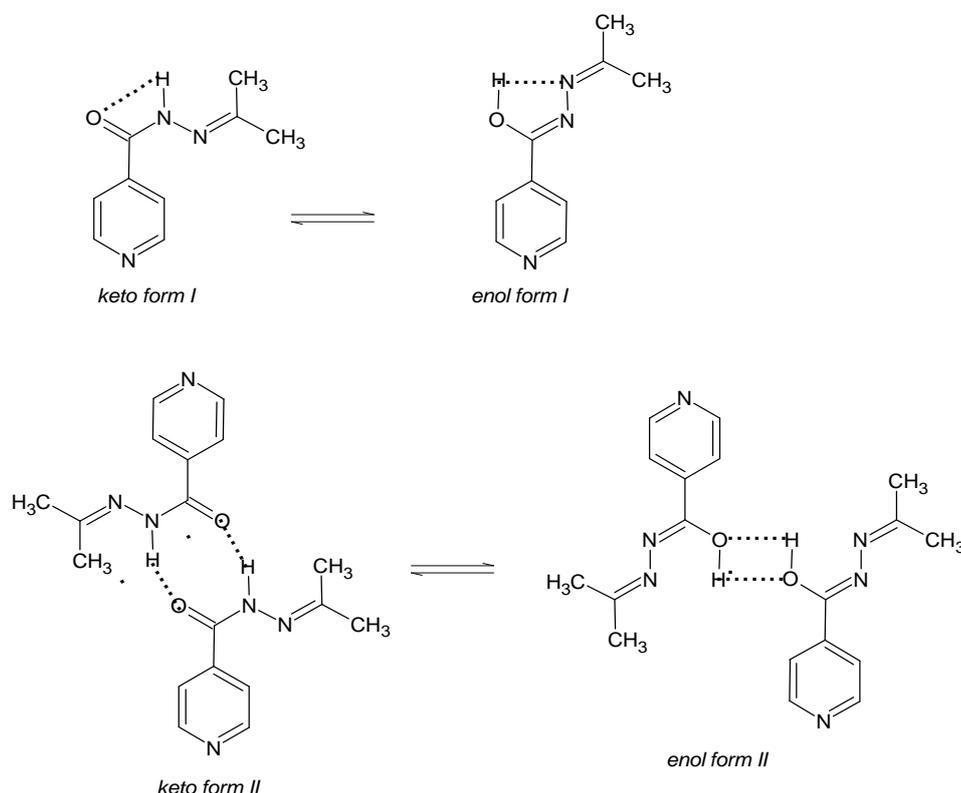
Scheme 2: Showing the possible mode of intramolecular and intermolecular hydrogen bonding in the ligands

Table 2a: Diagnostic IR bands for the ligands and complexes (cm⁻¹)

Compound	ν [OH]	ν [NH]	ν [C=O]	Δ [C=O]	ν [C=N]	Δ [C=N]	ν [O=U=O]	ν [M-N]	ν [M-O]
ANH		3302 3180	1650		1588				
1	3572	3267 3162	1595	-55	1547	-41	928	461	525
3	3320	3267 3160	1593	-57	1543	-44	924	458	529
AINH		3301 3183 3102	1666		1584				
2	3427	3313	1597	-69	1543	-41	936	466	501
4	3457	3152	1586	-80	1548	-36	920	466	510

Bands in complexes spectra shown in Tables 2a and 2c are indicative of the nitrate and acetate ions coordination. The nitrato complexes display three NO stretches (Table 2a) which is not unexpected for its C2v symmetry. The nitrate ion is known to coordinates to a metal centre as a unidentate, chelating bidentate and bridging bidentate ligand giving rise to different structures. Using vibrational spectroscopy to differentiate these structures may be quite unreliable mainly due to the very slight differences in the nitrate ions symmetry. The uranium metal analysis for these complexes however suggest unidentate mode of coordination considering the complexes geometry.

Table 2b: NO stretching frequencies and structures of the NO₃ complexes (cm⁻¹)

Compound	ν₅	ν₁	ν₂	ν₅ − ν₁
1 [UO₂(ANH)₃(NO₃)₂] 2H₂O	1608	1198	1122	411
2 [UO₂(AINH)₃(NO₃)₂] 3H₂O	1595	1208	1156	387

Table 2c: carboxyl stretching frequencies and structures of the carboxylate complexes (cm⁻¹)

Compound	νₐ[COO]	νₛ[COO]	Δ	Mode of coordination
3 [UO₂(ANH)₂(CH₃COO)₂] H₂O	1609	1152	457	unidentate
4 [UO₂(AINH)₂(CH₃COO)₂] 3H₂O	1607	1153	454	unidentate

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Bands in complexes spectra shown in Tables 2a and 2c are indicative of the nitrate and acetate ions coordination. The nitrato complexes display three NO stretches (Table 2a) which is not unexpected for its C_2v symmetry. The nitrate ion is known to coordinates to a metal centre as a unidentate, chelating bidentate and bridging bidentate ligand giving rise to different structures. Using vibrational spectroscopy to differentiate these structures may be quite unreliable mainly due to the very slight differences in the nitrate ions symmetry. The uranium metal analysis for these complexes however suggest unidentate mode of coordination considering the complexes geometry.

Unlike in the nitrato complexes, the bands assignment in the acetato complexes can be a useful diagnostic tool in the elucidation of the mode of the acetate ion coordination. In these complexes, the acetate ion displays v_a frequency bands at 1609 and 1607 cm^{-1} and v_s at 1152 and 1153 cm^{-1}, respectively. This is indicative of coordination of the carboxylate ion whose free v_a and v_s display at 1578 and 1414 cm^{-1}, respectively, since the bands are expected to be shifted to higher and lower frequencies for the v_a and v_s respectively when coordinated to a metal ion. The separation energies of 457 and 454 for the two complexes reveal unidentate mode of coordination (Nakamoto, 1997b).
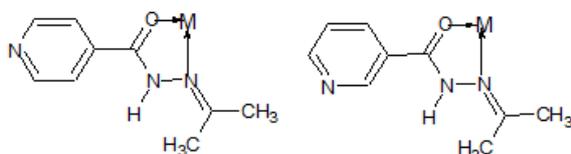
Scheme 3: Illustrating the involvement of the O and N atoms of the C=O and NH₂ respectively in coordination to the metal ion (M= UO²⁺)

Table 3: electronic spectra data

S/N	Compound	Band in DMSO
i	NH	390, 315, 285, 240
ii	1	490, 432, 385, 325
iii	3	440, 385,263
iv	INH	385, 320,245,235
v	2	490, 435,385, 360
vi	4	440, 362

Electronic spectra

The solution electronic spectra were taken in DMSO; data obtained is displayed in Table 3.

Those of the ligands show three set of peaks shown in Table 3 which are due to interligand charge transfer. These absorption bands were shifted to lower wavelength in complexes 2 and 3.
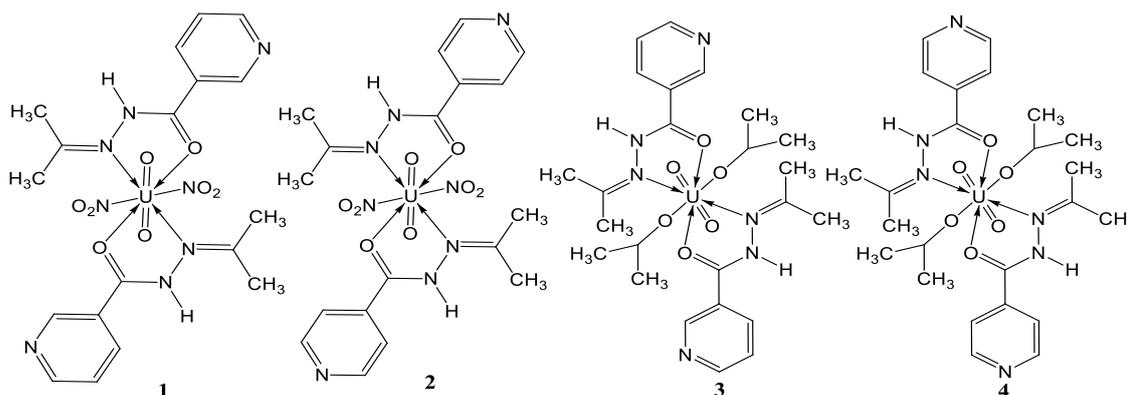
The peak position in complex 1 was relatively uninfluenced, while complex 4 was shifted to the red.

Since the UO_2^{2+} is an f^0 ion hence f-f transitions are not expected. Spectra of all four complexes display peak at between 477 – 323 nm which have been assigned to metal-ligand charge transfer transitions. A weak but sharp absorption band at 501 nm in complex 2 have been assigned to f-f transition, this band is too weak for assignment in the other complexes or might have tailed into the near infrared (NIR) region (Cotton and Wilkinson, 1972).

Antimicrobial studies

The result of the antimicrobial screening for the organic ligand molecule and the complexes are shown in Table 4.

Table 4: Antimicrobial Test Result

Compound	*S. aureus*	*E. coli*	*P. aeruginosa*	*C. albican*
ANH	-	-	++	-
AINH	-	-	+	-
1	++	+	-	+
2	-	-	-	-
3	++	+	+	+
4	-	-	-	-

++ Fair inhibition + Insignificant inhibition – No inhibition

ANH and AINH showed a fair and insignificant inhibition to the growth of *P. aeruginosa*. They were inactive against all other organisms tested. The metal complexes were expected to show improved activity over the ligands since chelation generally reduces polarity and increase the lipophilicity of the metal allowing for easier penetration of the bacterial lipid membrane (Djuikom *et al.,* 2016; Waleed *et al.*, 2013). This seems not to be the case with the studied complexes as they did not record any improvement in viability against *P. aeruginosa*. Except for a fair inhibition of the growth of the Gram-positive bacteria tested, *S. aureus*, all other microorganisms showed resistance to the action of the four complexes.

Conclusion

The acetone isonicotinic and acetone nicotinic hydrazones exhibited hydrogen bonding because of the presence of H, O and N functionalities in the molecules, these attributes can be utilized in molecular assembly with proper ligand design. The neutral ligands coordinate through the carbonyl O and the azomethine N atoms in the ligand forming a five-membered stable ring rather than through the pyridinic nitrogen while the nitrate and acetate molecules bind via unidentate mode. The structures in Scheme 4 are proposed for the complexes.

Scheme 4: The proposed structures for the neutral complexes

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Antimicrobial evaluation studies reveal that except *S. aureus* that was susceptible to complexes 1 and 3, all other microorganisms tested showed resistance to the action of the complexes. But because the bonds formed by the ligands in the current study form very stable complexes, which does not pass them as good candidate for dynamic libraries. Effort in this direction should be towards the utilization of low and medium weight hydrazones which can couple with carbonyl groups without forming stable bonds in hydrazone formation. These ligands may find application as uranyl ion extractant, useful candidate in uranium pollution remediation at milling and dump sites as well as in analytical chemistry.

Conflict of Interest

Author declares that there is no conflict of interest reported in this work.

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