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2-Aminobenzoyl Hydrazone Uranium(IV) Diacetate Complexes

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Introduction

Recently, there has been a growing interest in the syntheses of uranium(IV) complexes [1–5]. As a further contribution to this area, an attempt has been made to synthesize Schiff-base complexes of 2-aminobenzoyl hydrazones with uranium(IV) acetate. These compounds have been characterized by elemental analysis, conductivity, magnetic and infrared spectral data.

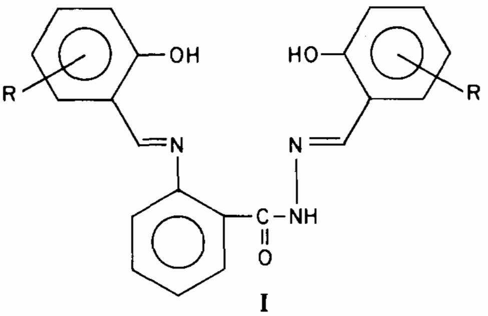
Experimental

All starting chemicals used in this work were of reagent grade.

The uranium(IV) acetate was prepared according to published methods [6]. 2-Aminobenzoyl hydrazide was prepared by refluxing 1.65 g of anthranilic acid with 1 g of hydrazine hydrate in 100 ml of ethanol for two hours. Upon cooling, the crystals precipitated and were recrystallized from ethanol.

The 2-aminobenzoyl hydrazone Schiff bases (**Ia–c**) were prepared by refluxing for 2 h a mixture containing 0.2 mol of substituted salicylaldehyde and 0.1 mol of 2-aminobenzoyl hydrazide in about 100 ml of ethanol. Upon cooling, the crystals of Schiff base were filtered and dried *in vacuo* over P_2O_5.

The uranium complexes were prepared by refluxing for 4 h a mixture of 0.01 mol uranium(IV) acetate and 0.01 mol 2-aminobenzoyl hydrazone Schiff base in 150 ml of dry benzene. Upon cooling, a green colored complex formed and was filtered and dried *in vacuo* over P_2O_5.



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(a) R = H
(b) R = 5-CH_3
(c) R = 5-Cl

The analytical and physical data for the complexes (Table I) agree with a 1:1 (metal diacetate:ligand) stoichiometry. The amorphous compounds are soluble in DMF, DMSO and pyridine but insoluble in nitrobenzene. The molar conductivities of 10^{-3} M solutions of the complexes in DMF as measured by an Elico-CM-62 conductivity bridge are in the range of 24–37 ohm^{-1} cm^2 mol^{-1} indicating some dissociation. IR data were recorded in KBR on a Perkin-Elmer Infracord spectrometer.

Results and Discussion

In the IR spectra of the ligands, a medium intensity band envelope at 3300–3200 cm^{-1} is observed and ascribed to the two phenyl hydroxy groups whereas a band at 2700 cm^{-1} is assigned to an intramolecular hydrogen-bonding OH moiety [7]. Upon complexation the band envelope at 3300–3200 cm^{-1} is shifted up to 3350 cm^{-1}, while the band at 2700 cm^{-1} disappears.

The hydrazones (**Ia–c**) may have both a keto and enol form [8]. If the ligand is in the keto form, ν(N–H) and ν(C=O) vibrations are observed whereas the absence of both these frequencies is characteristic of the enol form. In the free ligands, a band appears at 1640 cm^{-1} and is ascribed to ν(C=O).

A doublet at 1615 cm^{-1} observed in the ligands is due to ν(C=N). Upon complexation a singlet remains at 1615 cm^{-1}, and a new band appears at 1600 cm^{-1}. Apparently the Schiff base does coordinate to the uranium acetate through an azomethine nitrogen [9].

The 2-aminobenzoyl hydrazone uranium(IV) diacetate complexes exhibit two absorptions at 1570 and 1405 cm^{-1}. These bands do not appear in the hydrazone Schiff bases. The two bands are assigned to ν_{asym}(OCO) and ν_{sym}(OCO) respectively and attributed to the bidentate-coordinating acetate moieties attached to uranium [10].

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TABLE I. Analytical and Physical Data for the Uranium(IV) Complexes

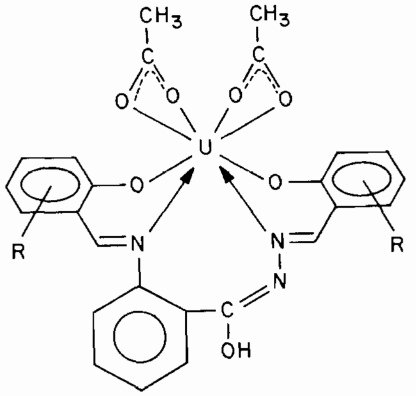
Ligand	Molecular formula of complex[a]	Yield (%)	Found (Calculated) (%)				μ_{eff} (B.M.)	λ (ohm^{-1} cm^2 mol^{-1})
			U	N	C	H		
a	$(C_{21}H_{15}N_3O_3)U(CH_3COO)_2$	58	32.49 (33.38)	5.58 (5.89)	40.36 (42.07)	2.71 (2.94)	2.95	37
b	$(C_{23}H_{19}N_3O_3)U(CH_3COO)_2$	56	31.39 (32.16)	5.47 (5.67)	41.51 (43.78)	3.35 (3.37)	3.06	33
c	$(C_{21}H_{13}N_3O_3Cl_2)U(CH_3COO)_2$	68	28.78 (30.20)	5.61 (5.32)	37.62 (38.07)	1.98 (2.41)	3.03	24

[a] All complexes decomposed above 300 °C and sharp melting points were not obtained.

A band at 1360 cm^{-1} in the ligands due to phenolic ν(C–O) is shifted to 1380 cm^{-1} in the complexes indicating the formation of a U–O bond. The bands at 621 and 520 cm^{-1} in the complexes are assigned to ν(U–N) and ν(U–O) respectively [1, 11–13].

The effective magnetic moments (μ_{eff}) for the uranium complexes as measured on a Gouy balance at room temperature are found to be around 2.95 to 3.06 B.M. corresponding to two unpaired electrons, and a triplet ground state ($^3H_4$).

Based on the foregoing arguments, it can be concluded that the environment around uranium(IV) consists of six O and two N atoms. Of the six oxygens, four belong to two acetate moieties. The uranium atom is likely to be above the plane of the ligand-coordinating atoms. We propose the following structure for the complexes in the solid state:



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