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TRANSITION METAL COMPLEXES DERIVED FROM N-ANTHRANILAMIDO-N'-BENZOYLTHIOCARBAMIDE (H₂ABTC)

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ABSTRACT

Complexes of N-anthranilamido-N'-benzoylthiocarbamide (H₂ABTC) with Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO₂(VI) have been synthesized and characterized on the basis of elemental analyses, molar conductivities, spectral (IR and visible) and magnetic studies. IR spectral data show that the ligand behaves in a neutral bidentate, mononegative bidentate or tridentate and binegative tridentate or tetradentate manner. All the complexes are non-electrolytes. Different stereochemistries are proposed for the Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) complexes according to the data of magnetic and electronic spectral measurements. IR data indicate that the carbonyl oxygen of the benzoyl moiety is the backbone of the chelating agent in all the complexes.

INTRODUCTION

Highly active antithyroid substances contain thiocarbamide moieties, NHCSNH, capable of being oxidized easily, and it has been suggested that interference with thyroxine synthesis results from direct reaction between I_2 and SH (formed by enolization) to form disulphides¹⁻³. Studies on metal complexes of (N-benzamido, N-salicylamido and N-isonicotinamido)-N'-benzoylthiocarbamide have been reported⁴⁻⁶. As an extension of our previous work and in order to understand fully the diverse coordinating properties and reactivity of this important class of ligands, we now report the synthesis and spectroscopic studies of transition metal complexes formed by the interaction between metal chlorides or acetates and N-anthranilamido-N'-benzoylthiocarbamide (Fig. 1).

EXPERIMENTAL

All chemicals used are of BDH quality (British Drug, LTD, England).

Synthesis of the Ligand

N-Anthranilamido-N'-benzoylthiocarbamide (H₂ABTC) was prepared by adding to anthranilic acid hydrazide (15.1 g, 0.1 mole) in 100 mL of a hot absolute ethanol benzoyl isothiocyanate (14.5 mL, 0.1 mole) dropwise with constant stirring. On cooling, yellowish white crystals were separated. The product was filtered off, washed with absolute ethanol and finally dried in a vacuum desiccator over anhydrous CaCl₂; yield 23.6 g (75%), m.p., 197°C.

Synthesis of Metal Chelates

The complexes $M(H_2ABTC)(OAc)_2.H_2O$ [M = Zn(II) or Cd(II)] and Ni(HABTC)(OAc).H_2O were prepared by adding a solution of 0.32 g (1 mmole) of H_2ABTC in 50 mL absolute ethanol to a solution of 1 mmole of metal acetate in 25 mL of bidistilled water. The mixture was heated under reflux for 1 hr. The UO₂(HABTC)(OAc).2H₂O complex was prepared by the same method using 0.39 g (1 mmole) of uranyl acetate in 25 mL of absolute ethanol and 0.32 g (1 mmole) of H₂ABTC in 25 mL of absolute ethanol. The Co(HABTC)₂ complex was obtained using 0.25 g (1 mmole) of the cobalt acetate in 25 mL of bidistilled water and 0.64 g (2 mmole) of H₂ABTC in 50 mL of absolute ethanol.

The binuclear $Cu_2(ABTC)(OAc)_2.4H_2O$ chelate was prepared by taking 0.4 g (2 mmole) of copper acetate in 50 mL of bidistilled water and 0.32 g (1 mmole) of H₂ABTC in 25 mL of absolute ethanol.

The complexes $Co(H_2ABTC)Cl_2.H_2O$, $Ni(H_2ABTC)Cl_2.4H_2O$ and $Cu(HABTC)Cl.C_2H_5OH$ were synthesized by mixing a solution of H_2ABTC (0.32 g, 1 mmole) in 50 mL absolute ethanol and a solution of 1 mmole of the metal chloride in 25 mL absolute ethanol. The mixture was heated under reflux for 2 hr. The Co(II) and Ni(II) complexes were precipitated after cooling by addition of diethyl ether. The Cr(ABTC)(OAc).H_2O complex was prepared by the same method in the presence of 0.82 g (10 mmole) of sodium acetate as a buffering agent.



Fig. 1. Structure of the Ligand (H₂ABTC)

The $Mn(HABTC)_2$ complex was prepared in the same manner as the Cr(III) complex but by using 0.64 g (2 mmole) of H₂ABTC.

The resulting solid complexes which formed during reflux were filtered off, washed several times with absolute ethanol followed by diethyl ether and finally dried in a vacuum desiccator over anhydrous $CaCl_2$.

The water of crystallization was determined from the mass loss by heating the complexes in an oven at 140°C for 5 hr.

Physical Measurements

The metal and chloride contents were analysed by standard methods⁷. Carbon and hydrogen were determined by the Microanalytical Unit of Mansoura University. Magnetic moments at 25°C were determined using a Gouy balance and Hg[Co(SCN)₄] as a calibrant. Electronic spectra in DMSO were recorded on a Perkin-Elmer 3B spectrophotometer. IR spectra were obtained using a Perkin-Elmer 1430 spectrophotometer in KBr discs. Molar conductivities in DMSO at 25°C were measured using a Tacussel conductivity bridge type CD6NG.

RESULTS AND DISCUSSION

The physical data of the complexes together with the elemental analyses and conductivities are listed in Table I.

The formation of the complexes may be represented by the following equations:

 $M(OAc)_2 + H_2ABTC \qquad \frac{Aqueous \ ethanol}{reflux \ l \ hr} \rightarrow M(H_2ABTC).(OAc)_2.H_2O \qquad (1)$ $(I) \qquad (I) \qquad (I) \qquad (I) \qquad (I) \qquad (I)$

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Table I. Analytical and Physical Data of H_2ABTC and its Metal Complexes.

Compound	Empirical formulas	Yield, %	Colour	M.P.,		% Cal	c. (Found)		$\Lambda_{\rm m}^{\rm a}$
	(Formula weight)	weight, g		ပ္	c	Н	М	Ð	
H ₂ ABTC	H ₁₄ C ₁₅ N ₄ O ₂ S (314.369)	73(23.6)	Yellowish white	197	57.3(57.0)	4.5(4.6)	•	•	,
Co(H ₂ ABTC)Cl ₂ .H ₂ O	CoH ₁₆ C ₁₅ N ₄ O ₃ SCl ₂ (462.215)	80(0.36)	Grey	>300	39.0(38.7)	3.5(3.4)	12.8(13.2)	15.3(15.5)	16
Ni(H ₂ ABTC)Cl ₂ .4H ₂ O	NiH ₂₂ C ₁₅ N ₄ O ₆ SCl ₂ (516.043)	75(0.33)	Yellowish	>300	34.9(34.7)	4.3(4.6)	11.4(11.6)	13.7(13.9)	22
Zn(H ₂ ABTC)(OAc) ₂ .H ₂ O	ZnH22C19N4078 (515.847)	70(0.35)	Pale yellow	>300	44.2(44.6)	4.3(4.1)	12.7(12.5)	•	6
Cd(H2ABTC)(OAc)2.H2O	CdH ₂₂ C ₁₉ N ₄ O ₇ S (562.877)	75(0.41	Pale yellow	>300	40.5(40.8)	3.9(4.2)	20.0(19.8)	•	7
Mn(HABTC)2	MnH ₂₆ C ₃₀ NgO ₄ S ₂ (681.662)	45(0.34)	Yellow	225	52.9(52.6)	3.8(3.8)	8.1(7.8)	•	11
Co(HABTC)2	CoH ₂₆ C ₃₀ NgO ₄ S ₂ (685.652)	65(0.52)	Grey	232	52.6(52.8)	3.8(3.9)	8.6(8.3)		6
Cu(HABTC)CI.C2H5OH	CuH ₁₉ C ₁₇ N ₄ O ₃ SCI (458.421)	70(0.32)	Olive gren	>300	44.5(44.8)	4.2(4.0)	13.9(13.6)	7.7(7.5)	18
UO ₂ (HABTC)(OAc).2H ₂ O	UH ₂₀ C ₁₇ N ₄ O ₈ S (678.469)	85(0.60)	Orange	>300	30.1(30.0)	3.0(2.8)	35.1(35.5)	•	9
Ni(HABTC)(OAc).H2O	NiH ₁₈ C ₁₇ N ₄ O ₅ S (449.133)	65(0.32)	Olive green	>300	45.5(45.8)	4.0(4.1)	13.1(12.9)	•	12
Cr(ABTC)(OAc).H ₂ O	CrH ₁₇ C ₁₇ N ₄ O ₅ S (441.415)	55(0.26)	Brown	>300	46.3(46.5)	3.9(3.7)	11.8(11.5)		80
Cu ₂ (ABTC).(OAc) ₂ .4H ₂ O	Cu ₂ H ₂₆ C ₁₉ N ₄ O ₁₀ S (629.589)	80(0.54)	Olive green	>300	36.2(36.6)	4.2(4.1)	20.2(19.8)		=
$^{\star} \Lambda_{m}$ is the molar conductivity	in DMSO at 25°C (ohm ⁻¹ cm ² mol ⁻¹)	1							

TRANSITION METAL COMPLEXES

Ni(OAc) ₂ + H ₂ ABTC	$\frac{\text{Aqueous ethanol}}{\text{reflux 1 hr}} \rightarrow$	Ni(HABTC)(OAc).H ₂ O + AcOH	(2)
2Сu(OAc) ₂ + H ₂ ABTC	$\frac{\text{Aqueous e thanol}}{\text{reflux 2 hr}} \rightarrow$	Cu ₂ (ABTC)(OAc) ₂ .4H ₂ O + 2AcOH	(3)
UO ₂ (OAc) ₂ + H ₂ ABTC	$\frac{\text{Absolute ethanol}}{\text{reflux 1 hr}} \rightarrow$	UO2(HABTC)(OAc).2H2O + AcOH	(4)
Co(OAc) ₂ + 2H ₂ ABTC	$\frac{\text{Aqueous ethanol}}{\text{reflux 1 hr}} \rightarrow$	Co(HABTC) ₂ + 2AcOH	[(5)
MCl ₂ + H ₂ ABTC	$\frac{\text{Absolute ethanol}}{\text{reflux 2 hr}} \rightarrow$	Co(H2ABTC)Cl2.H2O Ni(H2ABTC)Cl2.4H2O	(6)
CuCl ₂ + H ₂ ABTC	$\frac{\text{Absolute ethanol}}{\text{reflux 2 hr}} \rightarrow$	Cu(HABTC)Cl.C2H5OH + HCl	(7)
CrCl ₃ + H ₂ ABTC	$\frac{\text{Absolute ethanol}}{\text{CH}_{3}\text{COONa} + \text{H}_{2}\text{O}} \rightarrow$	Cr(ABTC)(OAc).H2O + 2HCl + NaCl	(8)
	reflux 0.5 hr		
MnCl ₂ + 2H ₂ ABTC	$\frac{\text{Absolute ethanol}}{\text{CH}_{3}\text{COONa} + \text{H}_{2}\text{O}} \rightarrow$	Mn(HABTC) ₂ + 2HCl	(9)
	reflux 0.5 hr		

All the metal complexes are stable in air and insoluble in common organic solvents but soluble in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). The molar conductivities (Λ_{m}) in DMSO at 25°C (Table I) indicate a non-electrolytic nature for the complexes⁸. The high values of the molar conductivities for some complexes suggest partial dissociation in DMSO.

Infrared Spectra

The most important IR bands in the spectrum of the free ligand as well as the bonding sites have been determined by a careful comparison of both the ligand and its metal complexes (Table II) and by considering our previous work⁴⁻⁶. The IR spectrum (KBr) of N-anthranilamido-N'-benzoylthiocarbamide (H₂ABTC) shows a doublet of bands at 3475

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Table II. IR Spectra of H₂ABTC and its Metal Complexes.

Compound	v(C=O)	v(C=0)	v(C=N)	v(C-O)	v(CS) + v(CN)) & v(C=S)	(N-N)^	(O-W)^	(N-W)^	(S-M)v	v(M-CI)
	Benzoyl	Anthranilamido									
H ₂ ABTC	1665	1620	,	1	1315	845	1020	•	•	-	•
[Co(H ₂ ABTC)Cl ₂] H ₂ O	1645	1620	•	ł	1295	835	1025	545	ŀ	350	265
[Ni(H ₂ ABTC)Cl ₂ .2H ₂ O].2H ₂ O	1645	1615	,	ı	1300	835	1020	535	•	335	265
[Zn(H ₂ ABTC)(OAc) ₂].H ₂ O	1650	1630	•	ł	1290	825	1020	535	•	335	,
[Cd(H ₂ ABTC)(OAc) ₂].H ₂ O	1650	1620			1280	820	1025	535	•	330	·
[Mn(HABTC) ₂]	,	1630	1585	1115	1305	830	1020	540	,	335	,
[Co(HABTC) ₂]	,	1625	1595	1115	1305	830	1020	540	•	350	ı
[Cu(HABTC)CI.C ₂ H ₅ OH]	'	1630	1600	1120	1300	835	1025	555	•	330	260
[UO2(HABTC)(OAc).2H2O]	1	1630	1585	1125	1305	830	1020	545	•	330	
[Ni(HABTC)(OAc).H2O]	1645	ı	1580	1115	1310	845	1035	555	455	1	,
[Cr(ABTC)(OAc).H ₂ O]	1	•	1590	1115	1315	845	1035	540	430		ı
[Cu ₂ (ABTC)(OAc) ₂].4H ₂ O	'	ı	1590	1120	1305	830	1040	545	430	345	I

and 3390 cm⁻¹ assigned to $v(NH_2)$ vibrations. The bands in the 3175-3360 cm⁻¹ region are assigned to the stretching vibration of NH groups. The two strong bands at 1665 and 1620 cm⁻¹ are attributed to the v(C=O)vibration of the benzovl moiety and the hydrogen-bonded anthranilamido moiety, respectively. Also, the two bands at 845 and 1315 cm⁻¹ are to v(C=S) and a combination of v(C=S) and v(CN), assigned respectively⁹. The band of relative medium intensity at 1025 cm⁻¹ is attributed to the v(N-N) vibration¹⁰. No bands exist above 3500 cm⁻¹ or in the 2500-2600 cm⁻¹ region which would be due to v(OH) and $v(SH)^{11}$ vibrations, respectively. The absence of these bands indicates the presence of H₂ABTC in the thione form. Two weak bands at <u>ca</u>. 1825 and <u>ca</u>. 2010 cm⁻¹ are assigned to the stretching and bending vibrations of (N-H...O). This may suggest the presence of intramolecular hydrogen bonding¹², as shown in Fig. 1.

complexes Co(H₂ABTC)Cl₂.H₂O, The IR spectra of the $Ni(H_2ABTC)Cl_2.4H_2O$ and $M(H_2ABTC)(OAc)_2.H_2O$ [M = Zn(II) or Cd(II)] show that H₂ABTC behaves as neutral bidentate ligand coordinating via the carbonyl oxygen (C=O) of the benzoyl moiety in the keto form and the thiocarbonyl sulphur (C=S) in the thione form, forming a six-membered ring including the metal atom. This mode of coordination is supported by the following evidence: (i) v(C=0) of the benzoyl moiety and v(C=S) shift to lower wave number; (ii) v(C=O) of the anthranilamido remains more or less at the same position, indicating that this group is not coordinated; (iii) the appearance of new bands in the regions 545-535, 350 - 330 and at 265 cm⁻¹ assignable to $v(M-O)^{13}$, $v(M-S)^{14}$ and $v(M-Cl)^{15}$, respectively.

In the Cu(HABTC)Cl.C₂H₅OH, UO₂(HABTC)(OAc).2H₂O and M(HABTC)₂ [M = Mn(II) or Co(II)] complexes, H₂ABTC acts as mononegative bidentate ligand, coordinating through the (C=S) in the thione form and the enolic carbonyl oxygen (=C-OH) of the benzoyl moiety with the displacement of the hydrogen atom from the latter group, forming a six-membered ring around the metal ion. This mode of complexation is confirmed by the following observations: (i) the disappearance of v(C=O) of the benzoyl moiety with the appearance of new bands in the 1125 - 1115 and 1600-1585 cm⁻¹ regions assigned to v(C-O)¹⁶ and v(C=N), respectively; (ii) v(C=S) shifts to lower wave number; (iii) the appearance of new bands in the regions 555-540 and 350-

330 cm⁻¹ and at 260 cm⁻¹ assigned to ν (M-O)¹³, ν (M-S)¹⁴ and ν (Cu-Cl)¹⁵, respectively. The Cu(HABTC)Cl.C₂H₅OH complex exhibits two bands at 3640 and 1190 cm⁻¹ assigned to ν (OH) and δ (OH) vibrations, indicating the participation of C₂H₅OH in bonding¹⁷ (Fig. 2).

Also, H₂ABTC behaves as a mononegative tridentate ligand in the Ni(HABTC)(OAc).H₂O complex, coordinating via the carbonyl oxygen of the benzoyl moiety in the keto form, the nitrogen atom of the NH group and the enolic carbonyl oxygen (=C-OH) of the anthranilamido moiety with the loss of the proton from the latter group. This mode of chelation (Fig. 3) is suggested by the following evidence: (i) the disappearance of v(C=O) of the anthranilamido moiety with the appearance of new bands at 1115 and 1580 cm⁻¹ assignable to v(C-O)¹⁶ and v(C=N), respectively; (ii) v(C=O) of the benzoyl moiety shifts to lower wave number; (iii) v(N-N) shifts to higher wave number; (iv) the appearance of new bands at 555 and 455 cm⁻¹ assignable to v(Ni-O)¹³ and (Ni-N)¹⁸, respectively.

In the Cr(ABTC)(OAc).H₂O complex, H₂ABTC behaves as a binegative tridentate ligand coordinating through the nitrogen atom of the NH group and both the enolic carbonyl oxygens (=C-OH) of the benzoyl and anthranilamido moieties with the abstraction of the hydrogen atoms from the enolized carbonyl groups. This behaviour (Fig. 4) is revealed by the following observations: (i) the disappearance of both v(C=O) vibrations with the appearance of new bands attributable to v(C-O)¹⁶ and v(C=N); (ii) v(N-N) shifts to higher wave number; (iii) the appearance of new bands at 540 and 430 cm⁻¹ assigned to v(Cr-O)¹³ and v(Cr-N)¹⁸, respectively.

Finally, the IR spectrum of the binuclear copper chelate, $Cu_2(ABTC)(OAc)_2.4H_2O$, shows that the ligand behaves in a tetradentate manner towards the two copper ions, chelating through the enolic carbonyl oxygen (=C-OH) of the benzoyl moiety and the sulphur of the (C=S) group from one end and the enolic carbonyl oxygen (=C-OH) of the anthranilamido moiety and the nitrogen of the NH group on the other end of the molecule with the replacement of the hydrogen atoms from the enolized carbonyl groups (Fig. 5). This mode of chelation is supported by the following evidence: (i) the disappearance of both v(C=O) with the appearance of new bands at 1120 and 1590 cm⁻¹ assignable to v(C-O)¹⁶ and v(C=N), respectively; (ii) v(C=S) shifts to lower wave number; (iii) v(N-N) shifts to higher wave number; (iv) the appearance of



Fig. 2. Proposed Structure of the Cu(HABTC)Cl.C₂H₅OH Complex



Fig. 3. Proposed Structure of the Ni(HABTC)(OAc).H₂O Complex

new bands at 545, 430 and 345 cm⁻¹ assigned to $v(Cu-O)^{13}$, $v(Cu-N)^{18}$ and $v(Cu-S)^{14}$, respectively.

All the acetate complexes show two new bands at <u>ca.</u> 1560 and <u>ca</u>. 1445 cm⁻¹ assignable to $v(C-O)_{as}$ and $v(C-O)_{s}$ bands of the acetate group¹⁹. The difference (115 cm⁻¹) between these two bands indicates a bridging or bidentate bonding mode for the acetate group.

The presence of water within the coordination sphere in the complexes [Ni(H₂ABTC)Cl₂.2H₂O].2H₂O, [Ni(HABTC)(OAc).H₂O], [UO₂(HABTC)(OAc).2H₂O] and [Cr(ABTC)(OAc).H₂O] is supported by the presence of bands in the regions 3460-3420, 1615-1600 (sh) and 980-960(w) cm⁻¹ in the spectra of these complexes due to OH stretching, HOH deformation and H₂O rocking¹⁹.

The uranyl complex exhibits three bands at 920, 840 and 250 cm⁻¹ assigned to v_3 , v_1 and v_4 vibrations, respectively, of the dioxouranium ions²⁰. The force constant (F) of v(U=O) is calculated by the method of McGlynn <u>et al.²¹</u> as 6.986 mdyne Å⁻¹. The U-O bond distance is calculated with the help of the equation²²:

$$R_{U-O} = 1.08 F^{-1/3} + 1.17$$



Fig. 4. Proposed Structure of the Cr(ABTC)(OAc).H₂O Complex



Fig. 5. Proposed Structure of the Cu₂(ABTC)(OAc)₂.4H₂OChelate

The U-O bond distance is 1.735 Å and falls in the usual region as reported earlier²³.

Magnetic and Electronic Spectral Studies

The magnetic moments and electronic spectral data of the complexes are depicted in Table III.

The electronic spectrum of Cr(ABTC)(OAc).H₂O exhibits three strong absorption bands at 18,870 (ν_1), 26,320 (ν_2) and 36,360 cm⁻¹ (ν_3) attributable to the ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ (ν_1), ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)$ (ν_2) and ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(P)$ (ν_3) transitions²⁴, respectively, in an octahedral environment around the Cr(III) ion. The ligand field parameters²⁵ and the magnetic moment (3.23 BM) confirm octahedral configuration.

The μ_{eff} value (6.13 BM) for Mn(HABTC)₂ is as expected for a high-spin 3d⁵ system. The electronic spectrum of this complex displays

Compound	Band position (cm ⁻¹)	Dq	В	β	^µ eff (BM)
[Cr(ABTC)(OAc).H ₂ O]	18,870, 26,320, 36360	1887	742	0.808	3.23
[Mn(HABTC) ₂]	23,810, 27,030			1	6.13
[Ni(HABTC)(OAc).H ₂ O]	16,390, 26,315	1034	780	0.749	2.82
[Ni(H2ABTC)Cl2.2H2O].2H2O	16,950, 27,030	1076	780	0.749	2.94
[Co(H2ABTC)Cl2].H2O	14,700				4.6
[Co(HABTC)2]	14,700				4.3
[Cu(HABTC)Cl(C ₂ H ₅ OH)]	15,870, 29,410				1.96
[Cu2(ABTC)(OAc)2].4H2O	14,705, 15,625, 27,780				1.52
[UO ₂ (HABTC)(OAc).2H ₂ O]	27,030				diam.

two bands at 23,810 and 27,030 cm⁻¹ which are clearly observed, indicating tetrahedrally coordinated $Mn(II)^{26}$.

The electronic spectra of the Ni(II) complexes show two bands in the 16,390-16,950 and 26,315-27,030 cm⁻¹ ranges assignable to ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ transitions²⁷, respectively. Also, the ligand field parameters (Dq, B, β) as well as the magnetic moment (2.82-2.94 BM) are consistent with octahedral geometry²⁸.

In the spectra of the Co(II) complexes the main band at 14,700 cm⁻¹ is attributed to the ${}^{4}A_{2} \rightarrow {}^{4}T_{1}(P)$ transition. Also, the magnetic moment (4.3-4.6 BM) can be taken as additional evidence for the tetrahedral structure around the Co(II) ions²⁹.

The electronic spectra of the Cu(II) complexes show one broad band with a maximum in the 14,705-15,870 cm⁻¹ range due to the ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition in a square-planar geometry³⁰. The band at 29,410 cm⁻¹ may be assigned to Cu \rightarrow Cl charge transfer³¹. Also, the μ_{eff} values (1.84-1.96 BM) lie within the range of Cu(II) ions. Finally, the UV spectrum of the UO₂(HABTC)(OAc).2H₂O complex shows a band at 27,030 cm⁻¹ attributable to the ${}^{1}\Sigma_{g}^{+} \rightarrow {}^{2}\pi_{u}$ transition for dioxouranium (VI)³².

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