

Some Complexes of Uranium Salts With Aromatic Compounds

A. A. Taqa
Department of Dental Basic Science
College of Dentistry
Mosul University

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الخلاصة

يتناول البحث تحضير وتشخيص بعض المعقدات الجديدة لأكسيد اليورانيوم السداسي باستخدام بعض المركبات الاروماتية كليكاندات. ان المركبات المستخدمة كليكاندات في هذا البحث هي الثايمول ، اليوجينول، مثيل الساليسيلات والكايكول. شخّصت المركبات المحضرة باستخدام المعلومات التي تم الحصول عليها من القياسات الفيزيائية والتي شملت التوصيلية المولارية للمعقدات في محلول غير مائي والتي دلت ان جميع المعقدات المحضرة هي معقدات متعادلة (غير ايونية). اظهرت دراسة طيف الاشعة تحت الحمراء للمعقدات المحضرة ان مجموعة التترات في اليورانيوم تتناسق بشكل ثنائي السن في هذه المعقدات. كما دلت نتائج البحث ان مركبات اليوجينول ، المثيل ساسيلات والكايكول تتاصر كليكاندات ثنائية التناسق.

ABSTRACT

This work deals with preparation and characterization of some new complexes of dioxouranium (VI) by using some aromatic compounds as ligands. The compounds used in this study were Thymol, Eugenol, Methylsalicylate and Gaiacol. Characterizations of these complexes are discussed, using information obtained from investigation of their physical properties. Conductivity measurements in non-aqueous solutions showed that all complexes were neutral (uncharged species or non-ionic). The infrared spectra indicated that the nitrate groups are coordinated as a bidentate in uranium nitrate complexes. The results also showed that (eugenol, methylsalicylate and gaiacol) coordinated as bidentate ligands.

INTRODUCTION

Eugenol (4-allyl-2-methoxyphenol), Methylsalicylate (methylhydroxy benzoate), Gaiacol (2-methoxyphenol) and Thymol (1-methyl-3-iso-propyl benzene) are importance clinically and pharmacological properties physio chemical characteristic. The acidity of phenols compared to alcohols can be accounted for by an argument similar to that used to explain the acidity of carboxylic acid. Conversion of phenol by loss of the hydroxyl proton to phenoxide anion is expected to lead to substantially greater delocalization of the unshared pair because of the resonance structure(1). Aromatic hydroxo compounds such as phenol readily from complexes that may have unidentate groups as in $[\text{W}(\text{Oph})_6]$, or have phenoxo bridge as in $[(\text{pho})\text{-TiCl}_2(\mu\text{-Oph})_2\text{TiCl}_2(\text{Oph})]$ (2).

Although an extensive literature is available on synthesis and structural characterisation of transition and non transition metals with phenolic compound (3-5), there is non previous work of these compounds with uranium salts. In the present paper are described the synthesis complexes of uranium (VI) nitrate, uranium(VI)acetate and uranium(VI) sulphate with eugenol, methylsalicalate, gaiacol and thymol. The coordination effects based on the infrared spectra and their characterization by analytical, conductance studies.

Experimental

The ligands used in this study thymol, methylsalicylate and gaiacol (Fluka company) and euganol(Dori Dent-Austria). All these chemical were of analar grade and used without further purification.

Molar conductance was obtained, on approximately 10^{-3} dimethylsulfoxide and chloroform solution using (Jenway PCM3 conductivity meter. Infrared spectra were recorded on a pye unicam SP2000 infrared spectrophotometer with $(200\text{-}4000\text{cm}^{-1})$ using CSI. Elemental analysis CH was carried out by Carlo Erba 1106 elemental analysis instrument.

Preparation of complexes

Preparation of uranium nitrate complexes

To a solution of (1×10^{-3}) mole $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in ethanol, a solution of ligand (2×10^{-3}) mol in ethanol was added with continuous stirring. The resulting solution was allowed to complete precipitation. The orange crystals were separated out and collected by filtration and finally washed with diethylether.

Preparation of uranium sulphate complexes

To a solution of (1×10^{-3} mol) $\text{UO}_2(\text{SO}_4)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ in ethanol, an ethanolic solution of (2×10^{-3} mole) ligand were added with continuous stirring. The resulting red solution was evaporated nearly to dryness, and a gum-like product appeared, was crushed in cold diethylether an orange crystal were obtained.

Preparation of uranium acetate complexes

To (5×10^{-4} mol) of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in ethanol added (1×10^{-3} mol) of ligand in hot ethanol, the yellow precipitation immediately formed as a fine powder. The product was separated by decantation, washed with diethylether then dried.

RESULTS AND DISCUSSION

The observed molar conductivities are tabulated in (Table1) measured at 10^{-3}M , indicating that all the complexes are non-electrolytes or uncharged species. Molar conductance values of the uranyl nitrate in chloroform (10^{-3}M) have been found to be below $4.4\text{cm}^2\text{ohm}^{-1}$ and thus depending non-electrolytic behaviour in this medium(3,6,7). However, the conductance values of these complexes in dimethylsulfoxide are in the range $108-140\text{cm}^2\text{ohm}^{-1}\text{mol}^{-1}$ which correspond 1:1 electrolyte. This shows that a coordinating solvent like DMSO is able to weakly coordinating nitrate group to a considerable extent in sufficient dilute solution as reported earlier (8-10). The UV/Visible spectra in 10^{-3} chloroform solution show a broad band observed in the range 360-400nm is due to $\pi \longrightarrow \pi^*$ transition of the free ligands, while a new additional band (Table1) was observed for all compounds in the range 360-400nm. This band can be attributed to the charge transfer transition from the filled ligand orbitals to the vacant metal orbitals.

The infrared spectra of the nitrate complexes show some bands of the nitrate frequencies,(Table2) a weak band in the region of $770-720\text{cm}^{-1}$ may be assigned to ν_5 , whilst ν_3 , a stronger band, sharper absorption, occurs in the region $745-760\text{cm}^{-1}$. The separation of these two frequencies is of the order $25-40\text{cm}^{-1}$ and similar values are reported previously (11, 12) for both monodentate and bidentate nitrate groups. A strong absorption in the region of $820-790\text{cm}^{-1}$ is assignable to ν_6 (11,13). The three absorptions ν_3 , ν_6 are thus assigned to the symmetrical bending of the two N-O bonds nearest the metal atom, the asymmetric bending of the same two bands, and out of plane rocking mode, respectively(11,12). Alternative assignments for these modes appear in

the literature(14). The symmetrical stretching frequency of the two N-O bonds nearest the metal atom, ν_2 , is in the range 1055-1040 cm^{-1} . A consideration of the bidentate nitrate group shows that the frequency occurring near 1550 cm^{-1} (1565-1520 cm^{-1}) is ν_1 , approximate to the stretching of the third oxygen atom and is thus symmetrical. The frequency near 1250 cm^{-1} (1270-1240 cm^{-1}), ν_4 , is assigned to the asymmetric stretching of two N-O bonds closet to the metal atom. The modes ν_1 and ν_4 are both strong and were found to be separated by 245-280 cm^{-1} for these complexes, hence the nitrate group appears to be bidentate in these complexes. However the size of this splitting is not a good criterion for distinguishing unidentate and bidentate nitrate group (11).

The overtone combination

Earlier studies (11,15,16) have assigned some of the over-tones and combination band for few uranyl nitrate complexes and they showed that the structural deduction for the nitrate groups may be made from such observations. (Table 2) shows some over-tone and combination bands for complexes studied in the present study. The assignments made largely follow theses of the earlier workers (11,17) The assignments made for $\nu_2 + \nu_5$, $\nu_2 + \nu_3$, $\nu_2 + \nu_1$ and $\nu_2 + \nu_4$ are good ones for the observed values for the fundamentals afford consistent comparison studied in this study. Curits et.al(15) show that the separation of $\nu_2 + \nu_5$ and $\nu_2 + \nu_3$ is greater in bidentate (approximately 30 cm^{-1}) than monodentate (approximately 10 cm^{-1}) nitrate complexes. Also they assignments the two frequencies observed between 2300 and 2600 cm^{-1} in the spectra of some monodentate and bidentate complexes to $\nu_2 + \nu_4$ and $\nu_2 + \nu_1$ respectively, and showed that the separation of these two frequencies is greater for bidentate (approximately 200-300 cm^{-1}) than for monodentate (approximately 90-200 cm^{-1}) nitrate groups. In the present study, the separation of $\nu_2 + \nu_5$ and $\nu_2 + \nu_3$ and also the separation of $\nu_2 + \nu_1$ and $\nu_2 + \nu_4$ are 35-40 cm^{-1} , and 260-325 cm^{-1} respectively. These values indicate that the complexes contain bidentate nitrate groups as reported earlier.(3,16-18).

The infrared spectra for the uranyl group vibration UO_2^{+2} (which have three vibration ν_1 , ν_2 and ν_3 , symmetric stretch, bend and asymmetric stretch) (Table2) show strong band in the region (945-910 cm^{-1}) attributed to ν_3 of uranyl group vibration. A weak and frequency appears between (880-830 cm^{-1}) which could not attributed definitely or excluded from being ν_1 . The infrared spectra for the acetate complexes (Table3) give bands in the region (1410-1430 cm^{-1}) and (1530-15550 cm^{-1}) and this attributed to ν_s and ν_{as} respectively. These values indicate that acetate

group coordinates as a bidentate in these complexes(19) The uranyl sulphate complexes also give three bands (Table3) for ν_3 (triple degenerate So strength) ν_4 (triply degenerated OSO bend) and one band for ν_1 (SO symmetric strength) and ν_2 (OSO symmetric bend). These indicate that sulphate group coordinated as a bidentate in these complexes(20,21)

It may be concluded that in these complexes, ligands act as monodentate (thymol) or bidentate(methylsalicylate, eugenol and gaiacol) and coordinate with uranium in all complexes, probably, more than six coordination number.

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Table (1) Physical measurements for the complexes

no.	Color	m.p C°	Empirical formula	Formula weight	Yield%	Analysis ^a C% H %	ϵ_{M} mol ⁻¹ cm ² mol ⁻¹ DMSO CHCl ₃	UV/Visible bands maximum in nm λ_{max} (nm) ϵ_{max} (dm ³ mol ⁻¹ cm ⁻¹)	ν_{UO_2} cm ⁻¹
1	Dark yellow	80	C ₂₀ H ₁₂ O ₄ .UO ₂ (NO ₃) ₂	720	82	33.33 (33.31) 3.055 (3.07)	134 0.7	390	930vs
2	Pale yellow	180d	C ₂₀ H ₂₂ O ₄ .UO ₂ SO ₄	692	65	34.68 (34.66) 3.17 (3.15)	113 2.4	370	930s
3	Dark yellow	150d	C ₂₀ H ₂₂ O ₄ .UO ₂ (CH ₃ COO) ₂	714	70	33.613 (33.64) 3.081 (3.10)	126 4.5	390	930s
4	Pale yellow	80	C ₁₆ H ₁₄ O ₆ .UO ₂ (NO ₃) ₂	692	82	27.58 (27.57) 2.01 (2.01)	118 2.8	400	910vs
5	Pale yellow	150d	C ₁₆ H ₁₄ O ₆ .UO ₂ SO ₄	668	70	28.74 (28.72) 2.09 (2.1)	135 6.8	370	945s
6	Dark yellow	95d	C ₁₆ H ₁₄ O ₆ .UO ₂ (CH ₃ COO) ₂	690	67	27.82 (27.84) 2.02 (2.04)	132 13.0	395	930s
7	Pale yellow	58	C ₁₄ H ₁₄ O ₄ .UO ₂ (NO ₃) ₂	640	85	26.25 (26.27) 2.18 (2.16)	140 6.3	380	940s
8	Dark yellow	84d	C ₁₄ H ₁₄ O ₄ .UO ₂ SO ₄	612	75	27.45 (2.42) 2.28 (2.28)	118 4.6	385	920vs
9	Dark orange	120d	C ₁₄ H ₁₄ O ₄ .UO ₂ (CH ₃ COO) ₂	634	76	26.49 (26.50) 2.20 (2.21)	135 27.6	380	940s
10	Dark orange	>350	C ₂₀ H ₃₀ O ₄ .UO ₂ (NO ₃) ₂	728	85	32.96 (32.98) 4.12 (4.11)	135 12.5	360	920s
11	Pale yellow	130d	C ₂₀ H ₃₀ O ₄ .UO ₂ SO ₄	700	75	34.28 (34.26) 4.28 (4.26)	120 15.0	390	920s
12	Pale yellow	160d	C ₂₀ H ₃₀ O ₄ .UO ₂ (CH ₃ COO) ₂	722	84	33.24 (33.24) 4.15 (4.17)	140 7.0	385	930vs

() found, d=decompose, vs=very strong, s=strong,

Table 2: Fundamental nitrate frequencies and over tones-combination vibrations for the nitrate complexes

No.	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	$\nu_2 + \nu_1$	$\nu_2 + \nu_4$	\wedge (cm)	$\nu_2 + \nu_3$	$\nu_2 + \nu_5$	\wedge (cm)
1	1560vs	1045vs	750vs	1265s	715s	850vs	2605	2310	295	1760	1795	35
4	1520s	1040m	745m	1260s	710vw	820vs	2560	2300	260	1750	1785	35
7	1665vs	1055s	760s	1240m	720s	750s	2620	2295	325	1775	1815	40
10	1550s	1050m	745s	1270s	710vs	790vs	2600	2320	280	1760	1795	35

W=weak, s=strong, vs=very strong, m=medium,

Table 3: The vibration frequencies infrared for the uranium sulphate and acetate complexes

No.	Uranium acetate complex		Uranium sulphate complex			
	ν_{sym}	ν_{asym}	ν_1	ν_2	ν_3	ν_4
2			960vs	470vs	1030m, 1150m, 1240s	600s, 640s, 650s
3	1400v	1570s				
5			975m	485s	1040w, 1080m, 1200w	600vs, 610s, 630m
6	1400vs	1560s				
8			-----	440m		600w, 610s, 650m
9	1410s	1530vs				
11			970s	-----	1030w, 1110w, 1210s	620w, 620s, 650s
12	1400w	1560vs				

W=weak, s=strong, vs=very strong, m=medium,

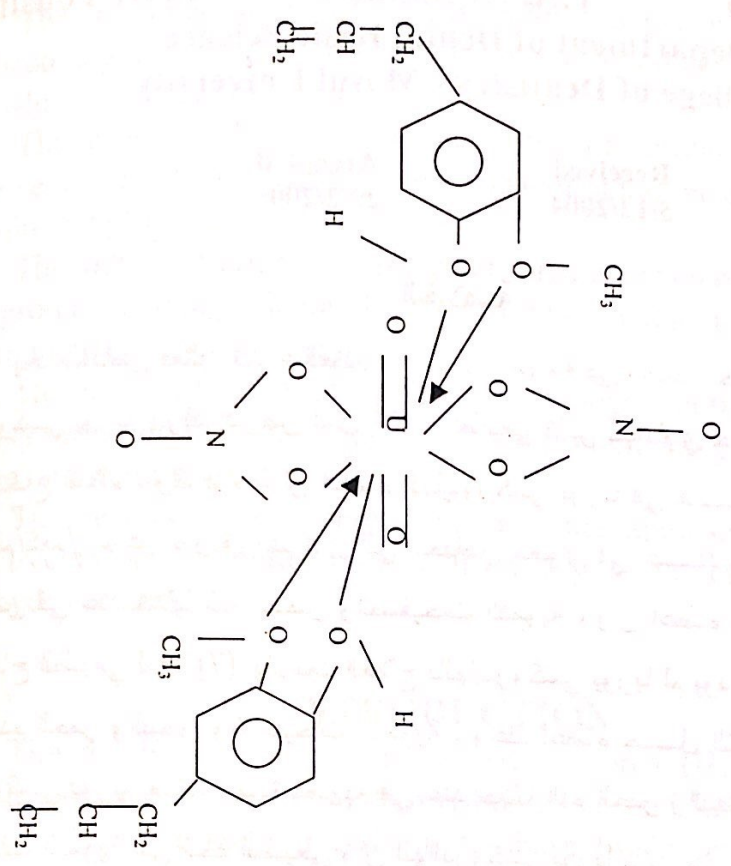


Fig 1: Suggest structure for uranium nitrate eugenolate the complex