COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME : 28 ANNÉE : 1982

Evidence For Five And Seven-Coordinate Uranium (VI)

by

M.A. WASSEF and L. ATYA

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Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

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Evidence For Five And Seven-Coordinate Uranium (VI)

M.A. WASSEF and L. ATYA

(Department of Chemistry, University College for Women, Ain Shams University, Heliopolis, Cairo, Egypt).

(Received 20 May, 1982, and accepted 6, October 1982)

SUMMARY

The infrared spectra of complex compounds of uranyl chloride-thiocyanate and -nitrate with thiazoles and oxazoles are reported. Complexes formed with the nitrate salt appear to have coordination number seven, while those formed with the chloride and thiocyanate have coordination number five.

INTRODUCTION

The uranyl cation UO_2^{2+} is the most common one among the hexavalent state of uranium. As regards to its coordination behaviour, it behaves as a single entity. In coordination compounds having the bipyramidal structure, the linear $O{=}U{=}O$ bonds of the uranyl group serve as an axis of symmetry while the other donor atoms form an equatorial polygon around it.[1]Other tetra-, penta-and hexa-gonal configurations are common for the uranium (VI) compounds.[2,3] Higher coordination numbers are also known.[4]

Coordination number five for uranium (VI), in which the complex has a trigonal bipyramidal configuration is rather rare.[5]

This work deals with the preparations and elucidation of the structure of the complexes formed between uranyl chloride, -thiocyanate and -nitrate with benzothiazole, 2-methylbenzothiazole, benzoxazole and 2-methylbenzoxazole.

Results And Discussion

The partial infrared spectral features of the complexes isolated in the present study are discussed. Tentative assignements of the bands are also indicated. Absorption bands in the range 4000-200 cm^{-1}due to coordinated thiazoles and oxazoles in the uranyl complexes which occur at almost the same frequencies as in the uncoordinated ligands are not listed. Contributions due to coordinate ligands were selected by comparing the ir spectra of uranyl complexes with that of the free ligands. The residual features in the case of thiocyanate and nitrate complexes were assigned to these groups and are as given in the text. Strong bands due to these group features are believed to superimpose and mask some of the ligand modes. Insolubility of these compounds precluded molecular weight and conductivity measurements.

The organic ligands used during the present work possess two potential sites of donation, nitrogen or oxygen and sulphur in the thiazole and oxazole rings, respectively. The complex compounds obtained were of a 1:1 mole ratio.

The spectra of these complexes are in good agreement with those of similar complexes of other metal salts, indicating coordination of the thinzoles ring through the nitrogen and the oxazoles ring through the oxygen atoms only.[6,7] Thus showing that these organic compounds act as monodentate ligands. This is in accordance with the fact that sulphur is considered to be a weak donor towards uranium (VI).[8]

Infrared studies show that these complexes possess coordination number five in the case of the complexes formed with uranyl chloride and thiocyanate, but in the case of the uranly nitrate complexes the coordination number is seven.

All the infrared spectra of the uranyl complexes under consideration show strong absorption bands at (910-950 cm^{-1}) and at (250-260 cm^{-1}) due to ν_3 and ν_2 modes, respectively, of the uranyl group.[9] No bands appear at $\sim$ 850 cm^{-1} due to ν_1 mode of the uranyl group ir forbidden in the freelinear OUO group, indicating that the linearity of the OUO group is maintained in these complex compounds. The doubly degenerate OUO bending vibration is observed at $\sim$ 270-230 cm^{-1} in the low frequency ir spectra and its frequency is consistent with similar mode in several other uranyl complexes.[10,11] The low frequency ir spectra of the uranyl complexes studied here show bands in the region 345-375 cm^{-1}. These bands are assigned as ir active uranium-oxygen streching modes in the benzoxazoles complexes.

Inspite of the heavy mass of the uranium atom the U-O mode in the present studied complexes occurs in almost the same frequency range as in other complexes reported for divalent transition metal with organic oxygen donating ligands.[12] The uranium-nitrogen stretching frequencies have been tentatively assigned by comparison with the spectra of the benzoxazole complexes, and are found in the range 290-310 cm^{-1}. Similar results are reported for palladium (II) complexes with thiazoles.[13] This suggests that the uranium-ligand bonding is quite strong in the complexes studied here.

Infrared spectra of the uranyl nitrate complexes show the presence of coordinated nitrate groups.[14] In metal complexes it is rather difficult to distinguish between monodentate and bidentate nitrate groups.[15] Ir frequencies associated with nitrato groups in these complexes occur almost at the same frequency ranges as in $UO_2(NO_3)_2$, $2H_20$[14] and other uranyl nitrate complexes[16,17] in which the presence of bidentate chelating nitrate groups has been established by infrared and X-ray structural studies. Presuming that the nitrate groups act as bidentate chelating ligands for the uranyl groups, the 1:1 uranyl nitrate complexes obtained in the present work may be considered to have seven-coordinated uranium with four oxygen atoms from two bidentate chelating nitrate groups and N or O atom from the ligands forming a ring around the U(VI) perpendicular to the OUO group.

Infrared spectra of the complexes formed with uranyl thiocyanate exhibit some new bands. These are identified as νCN (2055 and 2035 cm^{-1}), νCS (715 cm^{-1}) and νSCN (475 and 445 cm^{-1}) modes due to coordinated thiocyanate groups. The frequencies of these modes are in agreement with terminal S-bonded thiocyanate groups.[18] Thus, from a consideration of (a) 1:1 uranium: ligand ratio; (b) coordination of these ligands through oneatom only (N in the case of benzothiazoles and O in the case of benzoxazoles) and (c) the unidetate nature of the thiocyanate group, the complexes formed with uranyl thiocyanate presumably have five-coordinated uranium (VI) with three atoms (one nitrogen or oxygen from the ligand and two sulphurs of the thiocyanate groups) forming an equatorial ring perpendicular to the linear OUO group. Similar interpretation can be given for the uranyl chloride complexes.

EXPERIMENTAL

Infrared spectra were recorded in the range 200-4000 cm^{-1} on a Perkin-Elmer 471 in KBr discs. A Beckmann IR-12 instrument was used for recording the low energy vibrational spectra in the range 650-200 cm^{-1} in Nujol mull.

Benzothiazole, bt, 2-methyl-benzothiazole, 2-Me-bt, benzoxazole, bo and methyl benzoxazole 2-Me-bo, were obtained from Aldrich Chem. Co. Ltd. and used without further purification, the uranyl salts were BDH and the solvents used dried by conventional methods.[19] The complex compounds were simply prepared by mixing the uranyl salts and ligands in 1:1 molar ratios in hot ethanolic solution, refluxing for up to 1 hour, filtering, washing with ethanol and drying in vaccuo. Stoichiometry of the complexes isolated were checked by standard analytical methods[20] and gave satisfactory analyses. Uranium and chlorine were determined by volumetric method which is based on the work of Corpel and Regnaud.[21]

Compound	Found %		Calc. %	
	U	Cl	U	Cl
1. UO_2Cl_2, bt	48.8	14.6	50.0	14.9
2. $U0_2Cl_2$, 2-Me-bt	47.7	14.3	48.6	14.5
3. $U0_2Cl_2$, bo	48.5	14.9	49.8	14.8
4. $U0_2Cl_2$, 2-Me-bo	48.0	14.2	48.4	14.4
	U	SCN	U	SCN
5. $U0_2(SCN)_2$, bt	45.0	22.0	45.7	22.3
6. $U0_2(SCN)_2$, 2-Me-bt	43.8	21.2	44.5	21.7
7. $U0_2(SCN)_2$, bo	44.8	21.9	45.5	22.2
8. $U0_2(SCN)_2$, 2-Me-bo	43.6	21.0	44.3	21.6
	C	S	C	S
9. $U0_2(NO_3)_2$, bt	15.6	5.5	15.9	6.1
10. $U0_2(NO_3)_2$, 2-Me-bt	17.2	5.2	17.7	5.9
11. $U0_2(NO_3)_2$, bo	15.5	5.3	15.8	6.0
12. $U0_2(NO_3)_2$, 2-Me-bo	17.2	5.1	17.6	5.9

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Y.M. ISSA, A.M. HINDAWEY, H.Y.F.El-BARADIE,
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By

Y.M. ISSA, A.M. HINDAWEY*, H.Y.F.El-BARADIE
R.M. ISSA**

Chemistry Departement, Faculty of Science, Cairo Univ. Cairo Egypt

SUMMARY

The molecular complexes of some mono, di or trimethyl pyridines with chloranil (I), diclorodicyano-p-benzoquinone (II) and chloranilic acid (III) are prepared and investigated by ir and nmr spectroscopy. The spectral changes revealed that I or II yield molecular complexes involving $\pi - \pi^*$interaction only while those with III include as well a proton transfer from one OH-group of the acceptor molecule to the nitrogen atom of the pyridine nucleus. The effect of position and number of the CH_3- groups is also considered.

INTRODUCTION

Molecular complexes of the donor-acceptor type (D...A) were the subject of a vast number of investigations in the last few decades. Though many workers considered the molecular complexes of aniline derivatives[1-4], substituted benzenes[5-8]or condensed ring systems[9,10], yet few studies involved pyridine and its derivatives[5,11]. The molecular complexes of pyridine and few of its derivatives were isolated by Kross and Fassel[5] and investigated by ir-spectroscopy. The type of bonding and stability constants of trinitrobenzene complexes with a series of pyridines, including methyl pyridines, were determined using nmr-spectroscopy.[6].

In the present investigation, the molecular complexes of α,β or γ-picolines (a,b and c respectively), Lutidine (d) (2,6-dimethyl pyridine) and

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*Present Address: Chemstry Dept., Faculty of Science, Alexandria Univ.

**Present Address: Chemistry Dept., Faculty of Science, Tanta Univ.

collidine (e) (2, 4, 6-trimethyl pyridine) with chloranil (1), dichlorodicyano-p-benzoquinone (III) and chloranilic acid (III) are prepared and investigated by ir and H^1nmr spectroscopy.

EXPERIMENTAL

All chemicals used in the present work were pure laboratory grade B.D.H. products.

The molecular complexes were prepared by mixing a hot solution of the donor in ethanol (0.01 mol. in 5 ml) with a hot saturated solution of the acceptor (acetone for I and ethanol for II or III). The solid complexes separated immediately especially with chloranilic acid, or on standing. The solid complexes were then filtered off and purified by boiling with ethanol or recrystalisation, from the same solvent. The purified complexes were filtered off dried and analysed for their nitrogen and chlorine contents. Some compounds were subject to C and N_2 determination. The results of analysis are always in confirmity with those required for 1:1 (donor: acceptor) complexes.

The ir spectra of the donors, acceptors and their complexes were recorded on a Unicam SP 1000 infrared spectrophotometer using the the KBr Wafer snd Nujol mull techniques. The results in both cases were not much different. The H^1nmr spectra were obtained by the aid of the Varian 60 nmr spectrometer using d^6 dimethylsulphoxide as solvent and trimethyl silane as an internal stardard.

RESULT AND DISCUSSION

The acceptor used involve the non-acidic chloranil or dichlorodicyano-p-benzoquinone and the acidic chloranilic acid. The complexes of each type are considered separately since the changes are different in both cases.

A The infrared spectra:

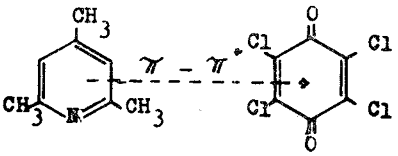
I. Spectra of complexes with I and II:

The spectra of molecular complexes of this class display apparent changes in the position of the absorption bands but neither original bands disappear nor new bands are observed. The main changes in the bands of the acceptor and donor parts of the molecular complexes are i-For the acceptor molecule, the C=0 bands at 1695 - 1678 cm^{-1}, the C=C bands at 1632 - 1558 $cm^{-1}$and the C-C bands at 1175 - 895 cm^{-1} are shifted to lower wavenumber as a result of the increased electron density on the acceptor in comparison to its free state. The same holds for the C≡N band of II.

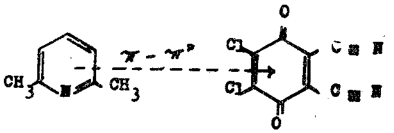
ii- For the donor part of the molecule, the band at 1630 - 1620 cm^{-1} corresponding to the C=N bond of the pyridine nucleus and the bands due to the various skeletal vibrations are shifted to higher wavenumbers. This is in accordance with the decreased electron density on the ring of the pyridine derivatives.

iii- the γCH bands of the free donor $\pi - \pi^*$ type[2,5].

Based on the above observations, the bonding between the donor and the acceptor molecules involves the location of a π - electron from the donor molecule to a π^*level on the acceptor one. The two components of the molecular complex are situated parallel to each other[9,10] which facilitates the π–π^*–electron interaction[2]. Accordingly, molecular complexes of I e and III d may be formulated as follows: Fig. (Ie) $<$ (IIId)



(I e)



(III d)

Though the lone pair of the pyridine nitrogen display a basic character, yet it is not liable that this lone pair contributes in an n - π^* interaction with the C=0 groups of I or the C=0 and C≡N groups of III. This is apparently due to low basicity of the pyridine nitrogen as a result of the participation of the n-electrons in a mesomeric shift with the π –clouds of the pyridine nucleus.

This is substantiated by the apparent shift of the C=0 and C≡N bands in the spectra of the molecular complexes to lower wavenumbers, while the bands corresponding to groups accepting an n electron are shifted to higher values[2-5]. Thus the bonding between the methyl pyridines under and chloranil or dichlorodicyano-p-benzoquinone in the molecular complexes would predominently involve π - π^*interaction. This result is in accordance with that observed for the pyridine-trinitrobenzene molecular complexes[11]as investigated by nmr spectroscopy.

II. Spectra of complexes with II:

The spectra of molecular complexes with chloranilic acid display marked changes in comparison to those of the free components, such changes are:

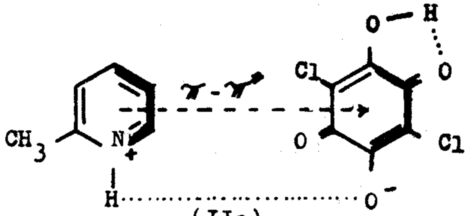
i- The OH-bands at 3235, 1270 and 1212 cm^{-1}corresponding to the weak hydrogen bonded OH-group of chloranilic acid are no more observed in the spectra of the molecular complexes. This denotes that the proton of this OH-group is involved in an interaction of the acid base type with the basic centre of the donor molecule i.e. the nitrogen atom of the pyridine nucleus. This is confirmed by the appearance of an intense group of bands within the 2800-2400 cm^{-1}range. These bands are assigned to the stretching modes of the structure ($=N^+$-H)[12], which is formed through a proton transfer from the acidic acceptor to the basic donor part of te molecular complex. This type of interaction leads to the so called complexes of the salt type[1,2] which involves an electrostatic attraction between the two components of the complex. The complex is further stabilised by the π – π^* interaction.

ii- The occurance of a π – π^*interaction is gathered from the shift of the C=0, C=C or C—C bands of chloranilic acid to lower wavenumbers which reveals an increased electron density on this part of the molecular complex.

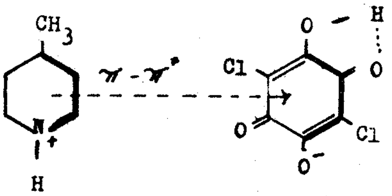
iii- The ν_{OH} and $\nu_{C\text{-}OH}$ bands of the remainder OH-group are shifted to lower wavenumbers while the δ_{OH} band is shifted to higher-values. These shifts denotes an increased strength of the intramolecular hydrogen bonding[1,3] in the C.T. complex. This recalls the behaviour of molecular complexes with polynitrophenols[2,3].

iv- The bands corresponding to the various vibrations of the CH_3 -groups are generally shifted to higher values due to the increased hyper conjugation between the CH_3-groups and the pyridine nucleus. This results from the decreased electron density on the pyridine derivative through the π - π^* interaction and the bonding of the proton to the nitrogen lone pair. The γ_{CH} bands of the pyridine nucleus are shifted to higher values indicating a decreased negative charge density on the donor molecule.

v- The bands due to the skeletal vibrations of the pyridine ring are mostly shifted to higher values due to the lowering of electron density on it through the $\pi - \pi^*$interaction. Based on the spectral changes observed, the bonding between the methylyridines and chloranilic acid can be given as follows; Fig. (II a) (II c)



(IIa)



(IIc)

B- The H^1 nmr spectra:

A substantial support for the results obtained from the ir spectra is gained by considering the changes of the H^1 nmr spectra of the molecular complexes under investigation in comparison to their constituents.

The H^1 nmr spectra of the donors display two sets of signals; the first one lies within the 2.6 - 2.3 ppm range and is due to protons of the CH$_3$-groups. The signal appears splitted in the spectrum of donor (e) due to the difference in the character of the three methl groups. The second set of signals corresponds to protons of the pyridine ring and occurs within the 7.6 - 6.9 ppm region. The spectrum of chloranilic acid (III) exhibits one signal at 8.1 ppm with integration equivalent to two protons coresponding to the OH-groups.

In the spectra of the molecular complexes with chloranilic acid, a new signal integration equivalent to one proton appears within the 3.8 - 3.1 ppm range. This signal can be assigned to the proton of the new center =N$^+$-H; this signal is shifted to higher values in the order (b → a → c → d → e) i.e. in the direction of increased basicity of the nitrogen atom of the pyridine nucleus. The proton transfer from teh acceptor to the donor is further supported by the decrease in the integration of the OH-signal of chloranilic acid in the spectra of the molecular complexes to a value almost equivalent to one proton. The OH-signal is slightly shifted to higher fields as a result of the increased strength of the intramolecular hydrogen bonding in the molecular complex.

The signals corresponding to the protons of the donor part of the complex are shifted to higher fields due to the decreased electron density on the pyridine ring which results from the intermolecular $\pi - \pi^*$ interaction with the acceptor part and the protonation of the pyridine nitrogen.

The H^1 nmr spectra of molecular complexes with I and II show obvious shifts of the donor signals to higher fields as a result of the intermolecular charge transfer interaction. However, the shifts observed with the complexes of I and II are of lower magnitude than for those with III, since the protonation of the nitrogen atom is not liable to occur with I and II.

It is worthy to mention that the magnitude of the band or signal shift, whether to lower or higher values, generally changes for one and the same acceptor on changing the donor in following order:

b → a, c → d → e which runs generally parallel to decreased ionisation potential of the pyridine derivative[14] As a matter of fact the π -ionisation potential decreases as the number of the donor CH_3-groups increases and hence the intermolecular π -bonding becomes stronger. The fact that the band shift runs almost in accordance with the ionisation potential of the donor molecules denotes that the increased number of the CH_3-groups displays rather little steric effects on the intermolecular interaction. This result is quite similar to that observed with complexes of p-benzoquinone with indol derivatives[15]. For the chloranil-alkyl benzene[16]complexes, it was found that the presence of the CH_3-group on the donor increased the stability of the molecular complex while the presence of C_2H_5- or C_3H_7- groups decreased its stability. Thus, the bulky groups cause steric effects on the approach of the two molecules (Forming the molecular complex while the methyl) group furnishes little steric effect.

TABLE I

Main bands of the acceptor in the ir spectra of the molecular complexes of methyl pyridines with chloro-p-benzoquinones.

Donor Colour	m.p. °C	ν_{OH}	$\nu_{=N\pm H}$		$\nu_{C=N}$	C=O	C=O	C=C	δ_{OH}	ν_{C-OH}	C—C	$\gamma_{CH donor}$
(1) Molecular complexes with chloranil:												
Bands of acceptor						1694	1682	1577			1112 907	
a olive green	270					1683	1670	1565			1112 910	1080. 890
b brown	213–233					1685	1675	1568			112 915	1080. 805
c black	270					1683	1672	1565			1112 910	1075. 900
d golden brown	270					1682	1670	1565			1110 908	1075. 890
e golden yellow	270					1680	1668	1563			1110 908	. .895
(2) Molecular complexes with chloranilic acid:												
Bands of free acceptor		3235							1270	1212	988 857	
		3170				1670	1635	1590	1290	1170	983 840	1075. 885
a dark violet	201	3150	2750	2600	2490	1670	1630	—	1292	1165*	983 842	1080. 880
b ,, ,,	187	2130	2840	2740	2530	1665	1625	1580	1290	1165*	980 842	1075. 897
c ,, ,,	195	3160	2730	2580	2470	1665	1632	1580	1292	1160*	982 845	1070. 885
d ,, ,,	194	3160	2750	2600	2470	1670	1632	—	α	1165	980 852	1070. 893
e ,, ,,	184	3180	2800	2690	2450	1670	1625	1570	1295	1167*		
(3) Molecular complexes with dichlorodicyano-p-benzoquinone: Bands of free acceptor					2225	1695	1678	1558			1175 895	
a dark brown	270				2210	1675*	1660	1540			1170 870	1080. 890
b ,, ,,	gummy				2205	1675	1655	1545			1170 875	1080. 900
c black	142				2210	1685	1670	1545			1165 890	1080. 905
d olive green	270				2205	1685	1670	1548			1165 892	1078. 900
e ,, ,,	185				2207	1675	1665	1550			1165 890	1055. 897

α interacting with neighboring bands,

* shoulder,

i interacting with neighbouring bands,

CH of free donor: 1070, 880 (a); 1075, 885 (b); 1070, 890 (c); 1065, 880 (d); 1045, 885 (e).

The CH_3-group generally functions as donor centre in virtue of its hyperconjugation with the π -electron system of the pyridine nucleus. With increased number of CH_3-groups, both steric factors and hyperconjugation rises in magnitude. However, the latter seems to be of dominant effect and hence the donor property increases and consequently the shift becomes higher.

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ACKNOWLEDGEMENT

The authors wish to thank Mr. Farouk Gaber (Tech. Assist.) for the aid he gave during the recording of the ir spectra.