

Studies on some Dioxouranium (VI) Complexes of N-Dimethylthioformamides Part II^{*}

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Summary: Dioxouranium (VI) complexes of N-dimethyl-thioformamide were prepared on treatment of uranyl chloride and uranyl nitrate with the ligand in 1:2 mole ratio in absolute alcohol. The complexes were characterised by IR spectroscopy and by their elemental analysis.

Introduction

Ambidentate ligands such as substituted thioureas are known to form a variety of complexes with transition metals [2,3]. For example it has been shown that in case of Pd(II), Pd(II) and Cu(I) the coordination is through N while in Zn(II) and Cd(II) it is through S atom [4].

We have recently reported such a behaviour with ligands like substituted thioureas, pyridine thiol and 2,4-dimethylpyrimidine thiol with transition metal carbonyls and dioxouranium salts [5,1].

In our continued research interest and to see the insight nature of bonding of these ligands the studies of complexes of dioxouranium (VI) and N-dimethylthioformamide were undertaken in which dioxouranium (VI) UO_2^{2+} ion acts as an electron acceptor.

Discussion

The Nature of NO_3 ion

The NO_3 ion of D_{3h} symmetry has four fundamental vibrations. Three of which $\nu_2(A_2)$, $\nu_3(E)$, $\nu_4(E)$ are IR active while $\nu_1(A)$, $\nu_3(E)$ and $\nu_4(E)$ are Raman active. On coordination its three fold symmetry is lost giving C_{2v} symmetry. Thus all the six normal modes of vibration become IR active. See Table 1.

The Nature of the UO_2^{2+} ion

The UO_2^{2+} ion has linear D_{∞h} symmetry with four normal modes of vibration. The non-degenerate symmetry stretching frequency is IR forbidden but is Raman active and it appears at 871 cm^{-1} in UO_2Cl_2 . While

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Table-1: The normal vibration modes of NO_3^- ION.

Point group	NO_3^- bonding	Assignment
D_{3h}	Ionic	$\nu_1(A_1) \nu_2(A_2) \nu_3(E) \text{IR} \nu_4(E) \text{IR}$
C_{2v}	Bidentate	$\nu_2(A_1) \nu_6(B1) \nu_1(A1) \nu_4(B2) \nu_3(A1) \nu_5(B)$

Table-II Analytical data

Compound		C	H	N	Colour
$\text{UO}_2\text{Cl}_2 \cdot 2\text{DMTF}$	Found (calcd.)	13.8 (13.6)	2.7 (2.5)	5.4 (5.2)	Yellow
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMTF}$	Found (Calcd.)	11.1 (10.4)	2.4 (2.2)	9.7 (9.2)	Orange Yellow

the non-degenerate antisymmetric stretching frequency ν_3 is IR allowed and occurs at 960 cm^{-1} [1,6]. Therefore the bands at 912 and 922 cm^{-1} were assigned for UO_2^{2+} ion in case of $\text{UO}_2\text{Cl}_2 \cdot 2\text{TMTU}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TMTU}$ respectively. These two bands were not observed in this region of the Raman spectra and instead bands at 820 and 840 cm^{-1} were reported. Thus the presence of bands at 910 cm^{-1} and 925 cm^{-1} in the IR spectra is of the complexes $\text{UO}_2\text{Cl}_2 \cdot 2\text{DMTF}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DMTF}$ may be assigned for UO_2^{2+} moiety, see Table III.

The Nature of (C=S) Stretching Frequency

The IR spectra of thioureas and substituted thioureas with transition metals have shown that due to the

internal ligand vibration it was difficult to assign metal to ligand mode of coordination. For example Lane and co-workers [2] have suggested that in case of N-methylthiourea its coordination to Zn(II) Cd(II) is through S atom. While in case of Pd(II) Pt(II) and Cu(I) it is through N atom. Two or three bands in the region of 1490 cm^{-1} of the ligand, only one band corresponds to (C=S) and the other are due to C-N modes. If one of the bands shows a decrease in frequency (say C=S) the other bands should show an increase in frequency. A band around 1120 cm^{-1} is said to contain C-N symmetrical stretching and N- CH_3 rocking character usually shows a small decrease in frequency. However, Schafer and Curran [7] have suggested that in tetramethylthiourea complex an increase in the frequency of 1504 cm^{-1} (which they claim is due to the N-C-N antisym, stretching vibration)

Table-III: IR spectra in KBR Pellet in cm^{-1}

Pure Ligand	$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DTF}$	$\text{UO}_2\text{Cl}_2 \cdot 2\text{DMTF}$
3519-3440	3590-3400(b.s)	3500-3000(b.s)
2940(m)	2930(w)	
1665(m)	1642(w)	1606(w)
1430(s)	1382(s)	1564(m)
1408(s)	1294(m)	1558(m)
1390(m)	1270(m)	1499(m)
1045(m)	1026(m)	1404(m)
	934(s)	1125(m)
	925(s)	944(m)
		910(m)

and decrease in the frequency around 1125 cm^{-1} which is due to C=S band indicate that ligand-metal coordination is through S atom. A similar trend was noticed in case of $\text{Mo}(\text{CO})_5 \text{L}^5$ and in this work. The far IR spectra of the complexes do not show uranium-sulphur stretching frequency which indicates that U-S bond is long, hence is a weak bond, (See Table III).

Finally the spectral evidence and the elemental analyses of the complexes (see Table-1) are consistent with the proposed formulations.

Experimental

Material

The dioxouranium salts $\text{UO}_2 \text{Cl}_2$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were obtained from BDH Chemical Ltd. U.K and N-dime-

thylthioformamide was purchased from Aldrich Chemical Co. Ethanol and other solvents were dried by conventional methods before use.

Physical measurements

IR spectra were measured in KBr pellets using a Perkin-Elmer Model 683 IR spectrophotometer.

Elemental Analyses

These were carried out by the Micro-analysis Laboratory of King Abdul Aziz University, Jeddah.

Preparation of the Compounds

Preparation of $\text{UO}_2\text{Cl}_2 \cdot 2\text{N}$ -dimethylthioformamide.

The complex was prepared by dissolving separately UO_2Cl_2 (1g. or 2.9 mole) and N-dimethylformamide (0.52 g or 5.8 mmol) in 1.2 mole ratio in absolute alcohol. The two solutions were mixed giving orange yellow solution. This was stirred for 1 hr at room temperature. The solvent was reduced to a minimum volume and left overnight which gave orange crystalline solid. This was washed twice with carbon tetrachloride and dried under vacuum.

Preparation of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{N}$ -dimethylthioformamide

The complex was prepared by following the same procedure as above, on treatment of the corresponding uranium salt (1g or 2 mmole) and the ligand (0.36 g or 4 mmole) in the 1.2 mole ratio. The resulting orange-red solution was stirred for 2 hour at room temperature. The solvent was reduced to minimum volume and left overnight, giving a red crystalline solid. This

was washed twice with carbontetra-
chloride and dried under vacuum.

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