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# Synthesis and Characterization of Mixed Ligand Complexes of Dioxouranium(VI) with Isatin-3-semicarbazone

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Some dioxouranium(VI) complexes have been synthesized with the Schiff base derived from indole-2,3-dione (isatin) and semicarbazone. Anions such as acetate, lactate, nitrate, perchlorate, sulphate and thiocyanate act as secondary ligands coordinating to the metal ion. Mixed ligand complexes with dimethyl sulphoxide or diphenyl thiourea and isatin-3-semicarbazone have also been synthesized. Physico-chemical properties of the complexes have been investigated by spectral analyses, molar conductance, molar mass determination and thermal analyses.

**Key Words: Dioxouranium(VI), Indole-2,3-dione, Semicarbazone, Dimethyl sulphoxide, Diphenyl thiourea.**

## INTRODUCTION

Coordination compounds offer variety of geometries and reactivity for use in drug design. Metal complexes of semicarbazones and thiosemicarbazones have aroused considerable interest in view of their industrial and biological importance. The chemical and biological activities of semicarbazones have been the subject of investigation in recent years. The biological activity is related to their action with metal ions. Schiff bases of isatin derivatives have shown different antimicrobial activity due to the different nature of the carbonyl and amino compounds as well as its substituent[1-3]. Isatin-3-semicarbazone (ISC) was used as the primary ligand and dimethyl sulfoxide (DMSO) or diphenyl thiourea (DPT) as secondary ligand in the preparation of dioxouranium(VI) complexes.

## EXPERIMENTAL

**Preparation of semicarbazone:** Isatin-3-semicarbazone was prepared by the condensation of isatin and semicarbazide hydrochloride in 1:1 molar ratio. They were separately dissolved in methanol, mixed well and refluxed on a waterbath for *ca.* 4 h. The resultant liquid mixture was concentrated and cooled to get bright yellow crystals of semicarbazone. It was separated, washed with petroleum ether, then recrystallized from methanol and dried *in vacuo* over phosphorus(V)oxide.

**Preparation of complexes:** Uranyl(VI) acetate dihydrate and isatin-3-semicarbazone in 1:2 molar ratio were separately dissolved in methanol, mixed well and refluxed on a water bath for *ca.* 6 h. The liquid mixture was concentrated and cooled to get the solid complex. It was washed with methanol followed by petroleum ether. The yellow coloured crystals were collected and dried *in vacuo* over phosphorus(V)oxide. Nitrato, lactato, perchlorato, sulphato and thiocyanato complexes were prepared by substitution of the anion from the acetate complex with the respective anionic salt solutions[4] *viz.*, $LiNO_3$, $C_3H_5O_3Li$, $LiClO_4{\cdot}3H_2O$, $Li_2SO_4{\cdot}H_2O$ and NaNCS in methanol in appropriate stoichiometric ratios. Mixed ligand complexes with dimethyl sulphoxide or diphenyl thiourea were prepared as follows. Uranyl(VI) acetate-dihydrate, isatin-3-semicarbazone and DMSO were reacted in 1:2:2 molar ratio. Methanolic solutions of uranylacetate, ISC and DMSO were mixed together and the mixture was refluxed on a waterbath for *ca.* 5 h. It was concentrated and cooled to get the solid complex. The crystals were washed with methanol followed by petroleum ether and dried *in vacuo* over phosphorus(V)oxide.

## RESULTS AND DISCUSSION

All the newly synthesized complexes are bright yellow or reddish brown in colour. They are non-hygroscopic solids soluble in acetonitrile, methanol and acetone but insoluble in benzene and diethyl ether. Molar conductance data reveal the non electrolytic behaviour of the complexes (Table-1). CHN analysis of the complexes is in agreement with the theoretical value calculated from the assigned formulae (Table-2). Molar mass of the complexes determined by Rast's method is also in agreement with the theoretical value obtained from the assigned formulae (Table-2). Important IR spectral bands of the ligand and the complexes along with their tentative assignments are given in Table-3.

TABLE-1
MOLAR CONDUCTANCE DATA OF DIOXOURANIUM(VI) COMPLEXES WITH ISC

| Complex | Conductance ($ohm^{-1}$ $cm^2$ $mot^{-1}$) | | |
|---|---|---|---|
| | Nitrobenzene | Methanol | Acetonitrile |
| $[UO_2(ISC)_2(NO_3)_2]$ | 7.25 | 10.12 | 14.23 |
| $[UO_2(ISC)_2(OAc)_2]$ | 1.28 | 8.56 | 15.68 |
| $[UO_2(ISC)_2SO_4]$ | 2.46 | 13.25 | 8.65 |
| $[UO_2(ISC)_2(NCS)_2]$ | 5.41 | 14.70 | 12.30 |
| $[UO_2(ISC)_2(C_3H_5O_3)_2]$ | 4.29 | 20.70 | 10.26 |
| $[UO_2(ISC)_2(ClO_4)_2]$ | 3.65 | 12.32 | 18.92 |
| $[UO_2(ISC)_2(DMSO_2)(OAc)_2]$ | 1.18 | 12.20 | 9.78 |
| $[UO_2(ISC)_2(DPT)_2(OAc)_2]$ | 6.70 | 6.28 | 12.01 |

IR spectra of isatin-3-semicarbazone exhibited a strong absorption band at 1707 $cm^{-1}$ attributed to the stretching vibration of >C=O group of isatin moiety. This absorption band is shifted to a lower frequency of 1675 $cm^{-1}$ in the spectra of the complexes with uranium suggesting that the >C=O group of isatin moiety is coordinated to the metal ion. The carbonyl group of semicarbazone was observed at 1680 $cm^{-1}$ in the spectra of the ligand while this absorption band is shifted to a lower frequency of around 1655 $cm^{-1}$ in the complexes indicating the corrdination of oxygen

TABLE-2
ANALYTICAL DATA OF DIOXOURANIUM(VI) COMPLEXES WITH ISC

| Complex | Molar mass: Found (calcd.) | Elemental analysis (%): Found (calcd.) | | | | | Anion (%): Found (calcd.) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | Cl | U | $NO_3^-$ | $SO_4^{2-}$ | $NCS^-$ |
| $[UO_2(ISC)_2(NO_3)_2]$ | 800.25<br>(802.36) | 26.18<br>(26.92) | 1.89<br>(2.01) | 17.96<br>(17.45) | – | 29.58<br>(29.67) | 14.86<br>(15.45) | – | – |
| $[UO_2(ISC)_2(OAc)_2]$ | 787.41<br>(796.36) | 33.04<br>(33.15) | 2.16<br>(2.78) | 14.24<br>(14.06) | – | 29.81<br>(29.89) | – | – | – |
| $[UO_2(ISC)_2SO_4]$ | 770.35<br>(774.29) | 27.45<br>(27.89) | 1.95<br>(2.08) | 14.38<br>(14.46) | – | 30.26<br>(30.74) | – | 11.91<br>(12.39) | – |
| $[UO_2(ISC)_2(NCS)_2]$ | 786.13<br>(794.12) | 30.13<br>(30.22) | 2.15<br>(2.03) | 17.38<br>(17.63) | – | 29.59<br>(29.97) | – | – | 14.15<br>(14.61) |
| $[UO_2(ISC)_2(C_3H_5O_3)_2]$ | 850.34<br>(856.36) | 33.27<br>(33.63) | 3.02<br>(3.06) | 13.41<br>(13.08) | – | 27.38<br>(27.79) | – | – | – |
| $[UO_2(ISC)_2(ClO_4)_2]$ | 873.40<br>(877.41) | 24.43<br>(24.62) | 1.65<br>(1.84) | 12.45<br>(12.76) | 7.86<br>(8.09) | 26.95<br>(27.13) | – | – | – |
| $[UO_2(ISC)_2(DMSO_2)(OAc)_2]$ | 948.73<br>(952.73) | 32.16<br>(32.75) | 3.48<br>(3.60) | 11.69<br>(11.75) | – | 24.56<br>(24.98) | – | – | – |
| $[UO_2(ISC)_2(DPT)_2(OAc)_2]$ | 1248<br>(1253) | 45.59<br>(45.97) | 3.46<br>(3.70 | 13.25<br>(13.41 | – | 19.03<br>(18.99) | – | – | – |

TABLE-3
IMPORTANT IR SPECTRAL BANDS OF ISC AND ITS COMPLEXES ($cm^{-1}$)

| ISC | $[UO_2(ISC)_2(OAc)_2]$ | $[UO_2(ISC)_2(NO_3)_2]$ | $[UO_2(ISC)_2(NCS)_2]$ | $[UO_2(ISC)_2SO_4]$ | Tentative assignments |
|---|---|---|---|---|---|
| 3470 | 3470 | 3468 | 3471 | 3472 | Asymmetric stretching of $-NH_2$ group |
| 3303 | 3302 | 3301 | 3303 | 3303 | Symmetric stretching of $-NH_2$ group |
| 3237 | 3237 | 3236 | 3236 | 3236 | N-H stretching of isatin moiety |
| 3131 | 3131 | 3130 | 3131 | 3131 | N-H stretching of semicarbazone |
| 1707 | 1675 | 1676 | 1675 | 1674 | >C=O stretching of isatin moiety |
| 1680 | 1655 | 1652 | 1652 | 1654 | >C=O stretching of semicarbazone |
| 1624 | 1590 | 1595 | 1595 | 1592 | >C=N stretching of azomethine |
| 1466 | 1467 | 1466 | 1466 | 1466 | C-N stretching of amide |

atom of semicarbazone. IR spectra of the ligand exhibited a sharp band of medium intensity around 1624 $cm^{-1}$ corresponding to the stretching vibration of >C=N group. In the spectra of the complexes, the >C=N stretching frequency shows a downward shift of 30-35 $cm^{-1}$, suggesting that the nitrogen atom of azomethine group is coordinated to the metal ion[5]. IR spectra of the ligand and the complexes show two sharp bands at 3470 and 3303 $cm^{-1}$ which are assigned to the asymmetric and symmetric stretching vibrations of $-NH_2$ group. Since there is no frequency shift in the spectra of the complexes the nitrogen atom of $-NH_2$ is not coordinated to the metal ion.

Absorption bands observed at 3237 and 3132 $cm^{-1}$ are attributed to the -N-H stretching of cyclic amido group and the semicarbazone moiety. These nitrogen atoms are not coordinated to the metal ion as these bands are observed at the same frequencies in the spectra of the complexes too. IR spectra of the complexes show U-O and U-N stretching vibrations at 530 and 420 $cm^{-1}$, respectively which further supports the coordination of oxygen and nitrogen atoms to the metal ion. Thus the IR spectral data revealed that the ligand ISC acts as a tridentate chelating agent coordinating through the oxygen atoms of carbonyl groups of isatin and semicarbazone moiety as well as through the nitrogen atom of azomethine group.

Coordination behaviour of anions in the complexes has also been ascertained from their IR spectra. Acetato complex exhibited two absorption bands at 1348 and 1592 $cm^{-1}$ which are attributed to the symmetric and asymmetric stretching vibration of $COO^-$ of coordinated acetate ion in a monodentate fashion. IR spectra of lactato complex also suggest monodentate coordination. Nitrato, thiocyanato and perchlorato compexes also exhibited monodentate coordination while sulphato complex exhibited bidentate coordination through oxygen atoms. Mixed ligand complexes with DMSO exhibited a sharp band around 1010 $cm^{-1}$ which is attributed to the stretching vibration of bonded S=O group of DMSO[6,7]. Mixed ligand complexes with diphenyl thiourea exhibited a sharp band at 1020 $cm^{-1}$ which is attributed to the stretching frequency of coordinated >C=S group.

Electronic spectra of ISC exhibited an absorption band at 202 nm due to the $\pi \rightarrow \pi^*$ transition of >C=O group. $n \rightarrow \pi^*$ transition of carbonyl group is observed at 253 nm while in complexes this transition occurred at 240 nm. The $n \rightarrow \pi^*$ transition undergoes a blue shift indicating that the lone pair electrons of oxygen are coordinated to the metal ion. As a result the energy of $\pi \rightarrow \pi^*$ transition is lowered and the absorption band is seen at a longer wavelength of 213 nm (red shift). Absorption bands observed at 269 and 319 nm in the spectra of ISC are attributed to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of >C=N group. Spectra of the complexes exhibit blue shift for $n \rightarrow \pi^*$ transition which is observed at 308 nm and red shift for $\pi \rightarrow \pi^*$ transition of >C=N group too, suggesting the coordination of nitrogen atom[8]. Absorption band observed around 400 nm in the spectra of the complexes is due to charge transfer transition from the ligand to the 5f/6d orbitals of uranium. Such charge transfer transitions are responsible for the bright colour of these complexes[5,8,9].

Thermal analysis of acetato complexes of uranium with isatin-3-semicarbazone were carried out in an atmosphere of air at a heating rate of 10 ºC/min. The TG curve revealed that the complex is stable upto 250 ºC. The complex exhibited a two stage decomposition pattern which started at 250 ºC and ended at 330 ºC during the first stage. A sudden mass change is observed from 400-500 ºC during the second stage. A plateau is observed in the TG curve beyond 500 ºC suggesting the stability of the final product, $U_3O_8$ (35.47 %) which is in agreement with the pyrolysis data (35.96 %) and the theoretical value (35.25 %) DTA peaks observed at 264 and 461 ºC confirmed this two stage decomposition process.

On the basis of these spectral and analytical investigations the following molecular formulae were suggested for the complexes.

$[UO_2(ISC)_2X_2]$, $[UO_2(ISC)_2Y]$, $[UO_2(ISC)_2(DMSO)_2(OAc)_2]$ and $[UO_2(ISC)_2(DPT)_2(OAc)_2]$ where 'X' represents monovalent anions such as acetate, nitrate, thiocyanate, lactate, perchlorate and 'Y' represents bivalent sulphate ion. Uranium exhibited a coordination number ten in its complexes with ISC while in the mixed ligand complexes with DMSO or DPT the coordination number was found to be 12.

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