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Spectral & biological characteristics of a novel Uranyl Proton transfer salt

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Abstract

The reaction of UO2$(NO_3)_2.6H_2O$ with the proton transfer compound obtained from 2,2'–dithiobis(benzoic acid) and 4–aminoantipyrine, ($HAAP^+.HTBA^-$), led to the formation of a novel complex of the formulae $[(HAAP)_2UO_2(HTBA)_2(NO_3)_2]$.This complex was characterized using IR, elemental, NMR and magnetic measurement along with the single crystal X–ray study of the ion pair. The anion is a six coordinated complex with an octahedral geometry around the UO_2(II) atom. UO_2(II) complex and ($HAAP^+.HTBA^-$) were screened for antibacterial properties and have exhibited potential activity.

Keywords: 4–aminoantipyrine, Uranyl, 2,2'–dithiobis(benzoic acid), XRD

1. INTRODUCTION

The different aspects of proton transfer systems have been studied by chemists in the recent years. Proton transfer attracts considerable attention because it plays a key role in a wide variety of biological and chemical phenomena [1]. Proton transfer in molecular association between carboxylic acids and Lewis bases confers considerable stability upon the structure making process, resulting generally in more hydrogen bonding associations particularly in systems involving the protonated amine functional groups. Fascinating molecular topologies and crystal packing motifs due to hydrogen bonding interactions are observed in the self assembly of various amines with carboxylic acids [2, 3]. Molecular association between 4–aminoantipyrine and 2–mercaptobenzoic acid, resulted in the formation of one such proton transfer salt, ($HAAP^+.HTBA^-$, Figure 1). In this compound 2,2'–dithiobisbenzoic acid , the oxidized product of 2–mercaptobenzoic acid acts as the proton donor and amino group of 4-aminoantipyrine is the proton acceptor. The flexible 2,2'–dithiobisbenzoic acid , a multifunctional ligand containing both carboxylic and thio groups, can potentially afford various coordination modes and coordination architectures [4, 5].

2. EXPERIMENTAL

2.1. Synthesis of proton transfer salt.

The compound $HAAP^+.HTBA^-$ was synthesized by refluxing equimolar amounts of 2-mercaptobenzoic acid and 4–amino antipyrine in 50% ethanol–water mixture for 15 h. Brown coloured blocks (M.P 224°C–225ºC), separated after partial room temperature evaporation of the solvent.

2.2. Synthesis of complex, $[(HAAP)_2UO_2(HTBA)_2(NO_3)_2]$

Equimolar solution of $UO_2\ (NO_3)_2.6H_2O$ in methanol (20 mL) was added to a stirring solution of proton transfer compound,($HAAP^+.HTBA^-$) in methanol-acetone mixture and refluxed for about 10h. The pale yellow solid complexes separated on slow evaporation of the reaction mixture was filtered, washed with methanol and dried.

3. RESULTS AND DISCUSSIONS

3.1 Single Crystal Structure of the proton transfer ion pair, ($HAAP^+.HTBA^-$)

The compound, ($HAAP^+.HTBA^-$) crystallizes in the space group P-1 with triclinic crystal system. The crystal structure reveals the formation of a 1:1 proton transfer compound held together by hydrogen bonds [5].

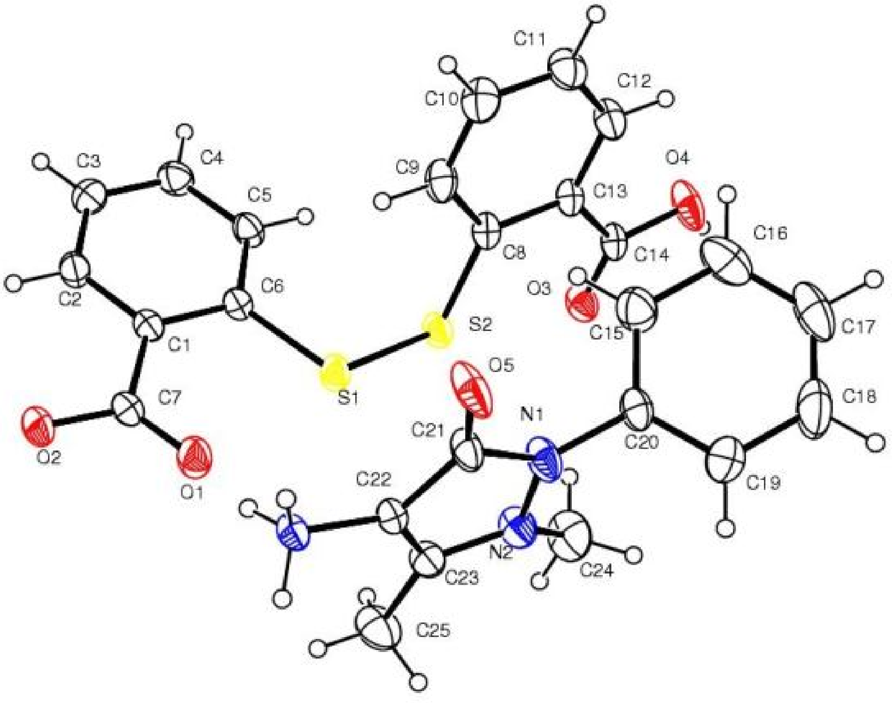

Fig. 1: Ortep diagram of ($HAAP^+.HTBA^-$)

The cation and anion moieties of ligand are held together by a combination of N–H…O and O–H…O hydrogen bonds. The presence of NH_3^+ is the source of extensive hydrogen bonds in the lattice. These non-covalent interactions form an extended ID supramolecular chain network.

3.2 Characterization of the complex, $[(HAAP)_2UO_2(HTBA)_2(NO_3)_2]$

The infrared spectrum of the ion–pair is characterized by a broad ammonium band centered at 3075 cm^{-1} along with bands at 1608 & 1492 cm^{-1} corresponding to the asymmetric and symmetric stretching vibrations of N–H bands of $NH_3\ ^+$[5]. The C=O stretch of the pyrazolone ring is observed at 1664cm^{-1} which remains as such in the complex also. The band corresponding to the stretching of carboxylic –C=O, which is observed as a superimpossible band along with the pyrazolone –C=O in the ligand spectrum is red shifted to 1697 cm^{-1} in the complex indicates the coordination of carboxylic –C=O. The presence of NH_3^+ bands without much shift in frequency in the spectrum of the complex confers that of the cation moiety does not involve in complex formation. Hence the coordination of the ion pair ligand to the metal occurs via the anion part only. A new strong peak at 1697 cm^{-1} shows an increase shift of the metal coordinated C=O of –COOH group of the anion moiety and a weak broad band around 3631 cm^{-1} shows the –OH stretching of the COOH group [5,6,7]. Another new band at 1630cm^{-1} confirms the coordinated COO^- group [8]. Also the strong peak at 1582 cm^{-1} in the ligand spectrum corresponding to COO– group is lowered to 1562 cm^{-1} in the spectrum of the complex due to metal coordination. Strong peaks at 1461 cm^{-1} and 1353 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of coordinated COO^- group [8]. A strong band characteristic of trans UO_2 is observed at 916 cm^{-1} which may be assigned to υ_{as} (O=U=O) and a medium intensity band at 856 cm^{-1} is assignable to υ_s (O=U=O) [6]. Two strong bands at 1220cm^{-1} and 1360 cm^{-1} with a separation of 140cm^{-1} corresponding to υ1 and υ4 and a medium band at 1024 cm^{-1} corresponding to υ2 of the nitrate group indicate the presence of terminal monodentate nitrate group [9].

Table 1: Characterization of ligand & the UO_2(II) complex

Compound	**Composition %found (calc)**			**μ$_{eff}$ (BM)**
	Carbon **Sulphur**	**Hydrogen**	**Nitrogen**	
$HAAP^+.HTBA^-$	62.15 (63.90) 10.06 (9.46)	4.13 (4.73)	12.01 (12.43)	–
$[(HAAP)_2UO_2(HTBA)_2(NO_3)_2]$	36.23 (35.50) 14.48 (13.56)	3.71 (3.57)	4.80 (5.60)	0

Table 2: FT-IR bands and tentative assignments of the ligand and UO_2(II) complex

Compound	**–C=O of COOH**	**N–H of NH_3^+**	**–C=O of pyrazolone**	**–COO– (asy)**	**–COO– (sym)**	**O=U=O (asy)**	**O=U=O (sym)**	**$\upsilon_{U–N}$**	**$\upsilon_{U–O}$**
$(HAAP^+.HTBA^-)$	1664	3075	1664	1582	1492	–	–	–	–
$[(HAAP)_2UO_2(HTBA)_2(NO_3)_2]$	1697	3064	1664	1560	1392	916	856	576	465

The NMR spectral data of the ligand and the complexes are given in Tables 3 and 4. The ^{1}H NMR spectra of the ligand is dominated by the presence NH_3^+, COO^-, COOH signals and the complex spectrum also shows the respective peaks with a slight shift. The ^{13}C NMR spectra of the complex also shows similarity towards the ligand except that there is a blue shift on the carboxylate –C=O and there is a red shift on the –C=O of carboxylic acid [10] indicates their coordinating to the metal.

Table 3: ^{1}H NMR chemical shifts of ligand and complex

$[HAAP^+.HTBA^-]$	**$[(HAAP)_2UO_2(HTBA)_2(NO_3)_2]$**	**Assignment**
2.103	2.231	C–CH_3
2.746	2.935	N–CH_3
7.222–8.045	7.185–8.558	Aryl protons
10.262	10.356	NH_3^+ of Pyrazolone
12.647	13.103	Carboxylic COOH

Table 4: ^{13}CNMR chemical shift of ligand and complex

[HAAP$^+$.HTBA$^-$]	[(HAAP)$_2$UO$_2$(HTBA)$_2$(NO$_3$)$_2$]	Assignment
9.82	10.305	C–CH$_3$
38.18	37.635	N–NH$_3$
119–138	120–141	Aryl carbons
161	160	–C=O of pyrazolone
167	163	–C=O of Carboxylate
170	176	–C=O of COOH

3.3. Antibacterial Studies

The antibacterial activity of the compound, (HAAP$^+$.HTBA$^-$) was evaluated by means of Disc Diffusion [11, 12] method against two gram positive bacteria namely *B. Cereus* and *S. Aureus* and two gram negative bacteria namely *V. Cholarae* and *S . Thyphimurium* and the results are discussed in the Table 5.

Table 5: Zone of growth of antibacterial activity

Compound	B. Cerus	V. Cholerae	S. Typhimurium	S. Aureaus
(HAAP$^+$.HTBA$^-$)	7 mm	9 mm	1 mm	2 mm
[(HAAP)$_2$UO$_2$(HTBA)$_2$(NO$_3$)$_2$]	10 mm	9.5 mm	2 mm	2.5 mm

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