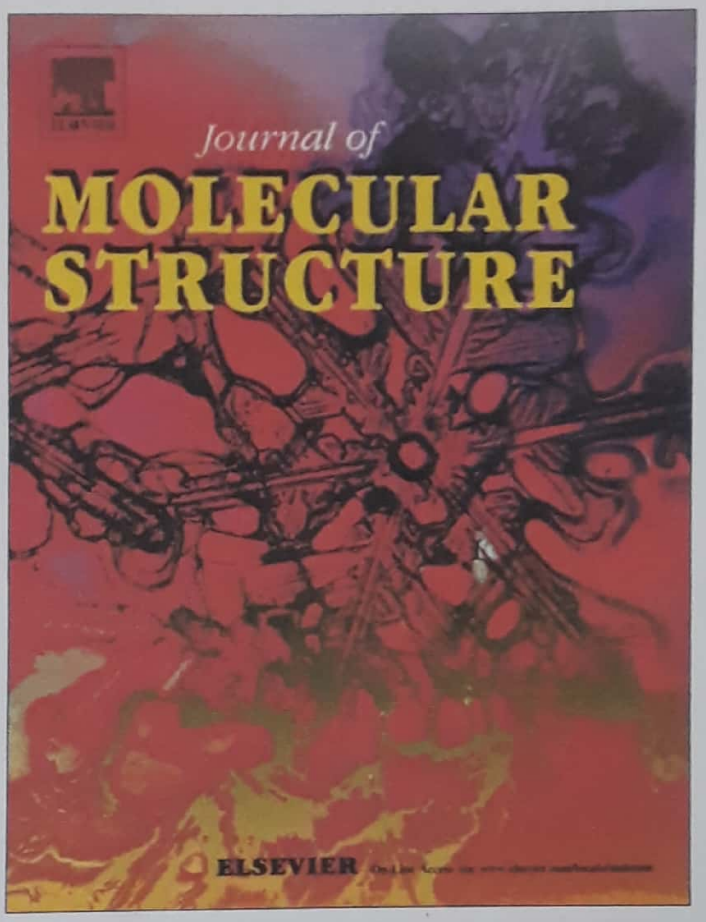

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Structural studies of 1-phenyl-2,3-dimethyl-5-oxo-1,2-dihydro-1*H*-pyrazol-4-ammonium 2[(2-carboxyphenyl) disulfanyl]benzoate

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HIGHLIGHTS

- The reaction between 4-aminoantipyrine and 2-mercaptobenzoic acid resulted in a proton transfer salt.
- This compound crystallize in the space group *P*-1.
- The ion-pair units are interlinked by hydrogen bonds forming a ID supramolecular network.
- Spectral studies (IR, NMR, Mass) confirm the formation of proton transfer salt.
- The compound shows thermal stability upto 260 °C.

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ABSTRACT

Reaction of 4-aminoantipyrine with 2-mercaptobenzoic acid afforded a proton transfer derivative, 1-phenyl-2,3-dimethyl-5-oxo-1,2-dihydro-1*H*-pyrazol-4-ammonium 2[(2-carboxyphenyl) disulfanyl]benzoate, ($HAAP^+ \cdot HTBA^-$), via the oxidation of 2-mercaptobenzoic acid into 2,2′-dithiobis(benzoic acid). The compound has been characterized on the basis of elemental analysis, IR, ^1H and ^{13}C NMR and mass spectral data. The infrared spectrum suggests the existence of an ion-pair compound, which is further established by the single crystal X-ray analysis to be an extended 1D supramolecular chain network extending along 'b' cell direction. The compound shows good thermal stability.

1. Introduction

Among the pyrazolone derivatives, 4-aminoantipyrine (AAP) has been used commonly as reagents in biological [1], pharmacological [2], clinical [3], and analytical applications [4]. Other derivatives of AAP such as schiff bases have been extensively investigated and utilized to construct metal-antipyrine networks in crystal engineering [5]. AAP offers both donor and acceptor sites for hydrogen bonding through amino N atom and keto O atom respectively. These non-covalent interactions play an important role in determining the potential applications of its analogues in material science [6] and pharmaceutical industry [7]. Recent research efforts have shown fascinating molecular topologies and crystal packing motifs due to N—H···O and O—H···O hydrogen bonded interactions in the self-assembly of various amines with carboxylic acids [8,9]. Similar non-covalent interactions leading to supramolecular networks are observed in the self-assembly of 4-aminoantipyrine with salicylic acid [10]. The crystal structure of the resulting compound showed charge assisted hydrogen bond interactions between protonated aminoantipyrine and a deprotonated salicylate anion. This observation prompted us to investigate the interactions between 4-aminoantipyrine and 2-mercaptobenzoic acid (MBA).

Herein, we report our results concerning the spectral and thermal studies along with single crystal X-ray analysis of the proton transfer salt, 1-phenyl-2,3-dimethyl-5-oxo-1,2-dihydro-1*H*-pyrazol-4-ammonium 2[(2-carboxyphenyl) disulfanyl]benzoate, ($HAAP^+ \cdot HTBA^-$), obtained during the reaction of 4-aminoantipyrine with 2-mercaptobenzoic acid.

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2. Experimental

2.1. Materials and physical measurements

4-Aminoantipyrine (Merck) and 2-mercaptobenzoic acid (Sigma–Aldrich) were of reagent grade and used as such. Microanalysis was carried out using a Vario EL III elemental analyzer. Infra red spectrum was recorded on a Perkin Elmer FT-IR instrument as KBr pellet in the range 4000–400 cm^{-1}. The ^1H NMR and ^{13}C NMR were recorded using Bruker DRX-500 MHz with DMSO as solvent. DART-MS was recorded on a Jeol-AccuToF JMS-T100LC mass spectrometer having a DART (Direct Analysis in Real time) source. The thermal studies were recorded on a Mettler TG-50 thermobalance with a heating rate of 20 °C/min, in nitrogen atmosphere. The single crystal X-ray data-collection of the compound was carried out using Bruker Axs kappa apex 2 CCD diffractometer.

2.2. Synthetic procedure

Refluxing 4-aminoantipyrine (0.203 g, 1 mmol) and 2-mercapto benzoic acid (0.308 g, 2 mmol) in 50% ethanol–water mixture for 15 h, followed by partial room temperature evaporation of the solvent, resulted in the separation of brown colored blocks of the compound, ($HAAP^+$·$HTBA^-$) with m.p. 224–225 °C (Scheme 1). The elemental analysis data for the compound, Found(Calcd): C,58.91(58.92); H,4.5(4.55); N,08.15(08.25); S,12.61(12.58) agrees with the empirical formula C_{25} H_{23} N_3 O_5 S_2.

2.3. Crystal structure determination of ($HAAP^+$·$HTBA^-$)

Single crystal suitable for diffraction was obtained by slow evaporation of a solution of the compound in ethanol–water mixture. The brown crystal of the compound having appropriate dimensions of 0.30 mm × 0.20 mm × 0.20 mm was mounted on a fine-focus sealed tube for X-ray crystallographic study. A Bruker Axs-kappa apex 2 CCD diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073) radiation was used for the measurement of data.

The structure was solved by direct methods and refined by full matrix least squares on F^2 (SHELXL 97) program package [11]. Molecular graphics employed include ORTEP 3 and Mercury 2.3. The hydrogen-atoms potentially involved in hydrogen bonding interactions were located from difference electron density maps. The positions of all H atoms were identified from a difference electron density peak and were fixed geometrically during refinement. The title compound crystallizes in triclinic *P*-1 with a = 9.6289(2) Å, b = 10.2473(2) Å, c = 13.7889(5) Å and V = 1203.12(6) A^3.

The crystallographic XRD data is given in Table 1. Full Crystallographic data (cif file) relating to the crystal structure have been deposited with the Cambridge Crystallographic Data Center as CCDC 764774.

3. Results and discussion

3.1. Single crystal structure of ($HAAP^+$·$HTBA^-$)

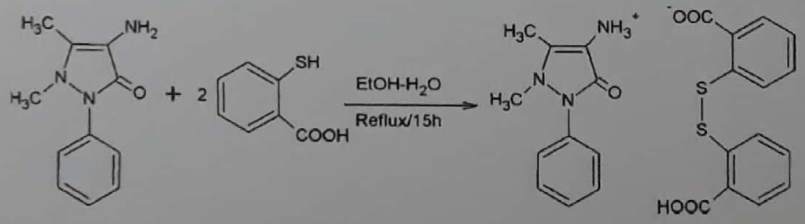
In the present study, during the 1:2 stoichiometric reaction of 4-aminoantipyrine with 2-mercaptobenzoic acid, the acid is first oxidized to 2,2′-dithiobis(benzoic acid), (H_2TBA) [12], which subsequently undergoes proton transfer to 4-aminoantipyrine to form an ion-pair compound, ($HAAP^+$·$HTBA^-$). The flexible conformation and variable degree of deprotonation of the dibasic acid (H_2TBA) is known to have formed cocrystals, with few bases, in which the acid–base pairs are held together by charge assisted hydrogen bonds [13].

The compound, ($HAAP^+$·$HTBA^-$), crystallizes in the space group *P*-1. The crystal structure reveals the formation of a 1:1 proton transfer compound, held together by a hydrogen bond. Here proton transfer takes place from the carboxyl group at C1 of the dibasic acid, (H_2TBA) to the amino group of the base, (AAP). The asymmetric unit of the compound thus contains 4-ammonium antipyrine, ($HAAP^+$) as the cation and monocarboxylate of 2,2′-dithiobis(benzoic acid), ($HTBA^-$) as the anion (Fig. 1). This is a redetermination of a similar crystalline structure isolated during the direct reaction of 4-aminoantipyrine with 2,2′-dithiobis(benzoic acid) [14].

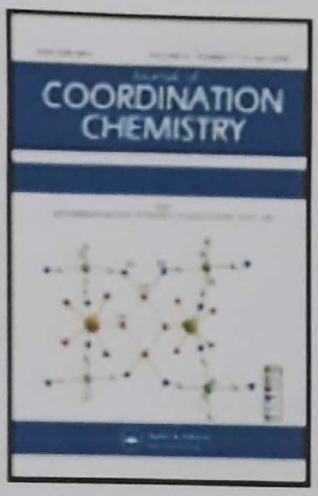
In the crystal of ($HAAP^+$·$HTBA^-$) obtained according to Scheme 1, the pyrazolone ring and phenyl ring are in gauche orientation along the N1—C15 bond. This is reflected from the dihedral angles C23/N1/C15/C20 = −66.0(3)° and C16/C15/N1/N2 = −65.6(3)°. Protonation of the amino group usually leads to the elongation of the C—N bond [15]. This is found true in the case of 4-ammonium antipyrine cation also. The C—N distance [C22—N3 = 1.4270(19) Å] is longer than the C—N distance of neutral AAP (1.3960 Å) [10,16]. This lengthening is observed when the amine N atom of AAP accepts a H atom from the carboxyl group of acid. All other bond length and bond angle values (Table 2) are consistent with those of other reported structure of AAP derivatives.

The anion moiety of the ion-pair is also non-planar. The S1—S2 bond length is 2.0502(6) Å and agrees with the literature value of other disulfides [17]. The dihedral angle value C2/S1/S2/C9 = 83.03(8)° shows that the aryl substituents on the two sulfur atoms are in an approximate perpendicular disposition with respect to each other [12]. The COOH and COO— groups are essentially coplanar with the respective aromatic ring. The benzene ring with COOH group is tilted more from the plane defined by the S1—S2 axis and the respective ring C atoms [S1/S2/C9/C10 = −16.12(15)°] than the other ring with COO— group [S1/S2/C2/C3 = −11.23(15)°]

There are two short non-bonded S···O contacts also [S1···O1 = 2.647 Å and S2···O3 = 2.665 Å] between sulfur atoms of disulphide linkage and oxygen atoms of COOH and COO— groups. The proton transfer from the carboxyl group at C1 to the neighboring amino group of pyrazolone moiety makes the C—C bond joining the COO— group [C1—C7 = 1.493(2) Å] to be slightly longer than that joining the COOH group [C8—C14 = 1.472(2) Å].



Scheme 1.



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Synthesis, spectral and magnetic studies of benzothiazolium tetrachlorocuprate salts: crystal structure and semiconducting behavior of bis[2-(4-methoxyphenyl)benzothiazolium] tetrachlorocuprate(II)

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Synthesis, spectral and magnetic studies of benzothiazolium tetrachlorocuprate salts: crystal structure and semiconducting behavior of bis[2-(4-methoxyphenyl)benzothiazolium] tetrachlorocuprate(II)

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Abstract

Reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with substituted 2-phenylbenzothiazoles and HCl in methanolic solution gave $(2\text{-PBZ})_2[CuCl_4]$, [2-PBZ = substituted 2-phenyl benzothiazolium]. Three such compounds, 2-(4-methoxyphenyl) benzothiazolium tetrachlorocuprate(II), $[(mpbH)_2CuCl_4]$, $(C_{14}H_{12}NSO)_2CuCl_4$; 2-(3-methoxy-4-hydroxyphenyl) benzothiazolium tetrachlorocuprate(II), $[(mhpbH)_2CuCl_4]$ $(C_{14}H_{12}NSO_2)_2CuCl_4$ and 2-(2-hydroxyphenyl)benzothiazolium tetrachlorocuprate(II), $[(hpbH)_2CuCl_4]$ $(C_{13}H_9NSO)_2CuCl_4$ were isolated and characterized by spectral and thermal studies. Single crystal analysis of bis[2-(4-methoxyphenyl) benzothiazolium] tetrachlorocuprate(II) $[(mpbH)_2CuCl_4]$ reveals that it crystallizes in P-1 space group with square planar $CuCl_4^{2-}$ and almost planar 2-(4- methoxyphenyl)benzothiazolium cation ($mpbH^+$). The discrete $CuCl_4^{2-}$ units are held between layers of 2-(4-methoxyphenyl) benzothiazolium, ($mpbH^+$) units, mainly by ionic and hydrogen bonding, resulting in a 3D

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Synthesis, characterization, biological & optical properties of a novel Mg(II) complex of a proton transfer ion pair salt

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Aliphatic or aromatic dicarboxylic acids represent supramolecular connectors that can generate infinite high-dimensional networks as ion-pairs, through complementary hydrogen bonds, involving a variety of basic building blocks such as amines, dipyridines and pyrazines. Such composite molecular aggregates often possess specific structures and activities due to the interplay of non-covalent interactions such as hydrogen bonding, π-π stacking, C-H-π and metal-π interactions. These ion-pairs or proton transfer salts form the basis of various biological processes which are very sophisticated and complex. The reaction of $Mg(Cl)_2 .6H_2O$ with the proton transfer compound obtained from 2,2'-dithio bis(benzoic acid) and 4-aminoantipyrine, ($HAAP^+.HTBA^-$), led to the formation of a novel complex of the formulae $(HAAP^+)_2 [Mg(TBA)_2]^{2-}$ .This complex was characterized using IR, elemental, conductance, NMR(^1H and ^{13}C) and mass spectral measurements 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 Mg(II) atom. Mg(II) complex and ($HAAP^+.HTBA^-$) were screened for antibacterial properties and non- linear optical studies and have exhibited potential activity.

Keywords: Proton transfer, ion-pair, aminoantipyrine, antibacterial, non-linear optical

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 [1-5] .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[6-8].

Results and Discussion

The single crystal study of the proton transfer salt reveals that, the compound, ($HAAP^+.HTBA^-$) crystallizes in the space group P-1 with triclinic crystal system. The crystal structure shows the formation of a 1:1 proton transfer compound held together by hydrogen bonds[9].

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. The Infrared spectra of the ligand and the complex were presented in **table 1**.

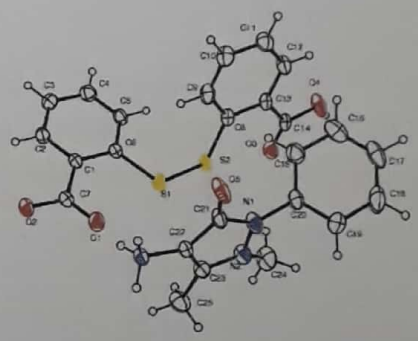

Figure 1: ORTEP diagram of ($HAAP^+.HTBA^-$)

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^+ [6]. The C=O stretch of the pyrazolone ring of cation is observed at 1664cm^{-1}, which remains as such in the complex also. 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[7-9] . A broad band centered at 3231cm^{-1} in the spectrum of ($HAAP^+ HTBA^-$), assigned to the stretching of hydrogen

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bonded O-H of the COOH group is also not observed in the spectrum of complex[6]. Hence it is confirmed that deprotonation of the COOH group has occurred thereby forming a dianionic species. Moreover a new band at 1630cm^{-1}confirms the coordinated COO^- group[10-12] . Strong peaks at 1415 cm^{-1} and 1375 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of coordinated COO^- group[11]. The presence of additional band at 432 cm^{-1} corresponds to the M-O stretching vibration. Conductance measurement of the complex in methanol solution (10^{-3}M) reveals the non- electrolytic nature of the complex[13].

The ^{1}H NMR and ^{13}C NMR spectrum of the ligand and the complex are presented in tables 2 & 3 .The ^{1}H NMR spectrum of the complex confirms the presence of NH_3^+ of cation moiety and the ^{13}C NMR spectrum confirms the –COO- coordination in the complex.

Table1: Significant FT-IR bands & tentative assignments of the ligand and the Mg (II) complex

Compound	$(HAAP^+.HTBA^-)$	$(HAAP^+)_2[Mg(TBA)_2]^{2-}$
N-H of NH_3^+	3075	3070
-C=O of pyrazolone	1664	1664
-COO-(asy)	1560	1415
-COO- (sym)	1420	1375
Mg-O	-	432

Mass Spectral studies

In the mass spectrum of $(HAAP^+)_2[Mg(TBA)_2]^{2-}$, the base peak corresponds to that of $(HAAP^+.HTBA^-)$ moiety (m/z at 509.5). m/z at 1042.7 corresponds to the molecular ion peak. Fragment peak at m/z 608.2 corresponds to that of the $(TBA)_2$ moiety. Another fragment peak at 837.1 corresponds to the $[M-C_{11}H_{14}N_3O]^+$ moiety[14].

Experimental section

Elemental analysis were carried out on a Vario EL-III CHNS Elemental Analyser at the SAIF,CUSAT,India..The NMR spectra were recorded using Bruker DRX-500 NMR spectrometer at SAIF, CUSAT, India. Antibacterial studies were done at C.E.P.C, Kollam, Kerala and NLO properties were studied at IISc, Bangalore, India.

Synthesis of Proton Transfer salt, $(HAAP^+.HTBA^-)$

The compound $(HAAP^+.HTBA^-)$ was synthesized by refluxing equimolar amounts of 2-mercaptobenzoic acid and 4-amino antipyrine in 50% ethanol-water mixture for 15hrs. Brown coloured blocks (M.P 224°C- 225°C), separated after partial room temperature evaporation of the solvent. The elemental analysis data for the ligand: Found (Calcd): C,58.92 (58.90); H,4.55 (4.53); N,08.25 (08.43) S,12.58 (12.46).

Table 2: ^{1}H NMR chemical Shifts of ligand & complex

$[(HAAP+.HTBA-)]$	$(HAAP^+)_2[Mg(TBA)_2]^{2-}$	Assignment
2.103	2.231	C-CH3
2.746	2.935	N-CH3
7.222-8.045	7.185-8.558	Aryl protons
10.262	10.351	NH3+ of Pyrazolone
12.647	-	Carboxylic COOH

Table 3: ^{13}CNMR chemical shift of ligand & complex

$[(HAAP+.HTBA-)]$	$(HAAP^+)_2[Mg(TBA)_2]^{2-}$	Assignments
9.82	10.1	C-CH3
38.18	40.25	N-NH3
119-138	120-141	Aryl carbons
161	161	-C=O of pyrazolone
167	163	-C=O of Carboxylate
170	-	-C=O of COOH

Synthesis of complex, $[(HAAP^+)_2[Mg(TBA)_2]^{2-}$

Equimolar amounts of $Mg(Cl)_2.6H_2O$ and proton transfer compound, $(HAAP^+.HTBA^-)$ in methanol-acetone mixture was refluxed for about 10hrs. The pale yellow solid complex which separated out on slow evaporation of the reaction mixture was filtered, washed with methanol and dried. The elemental analysis data for the complex is, Found (calc): C, 56.12 (56.08); H, 4.72 (4.70); N,7.80 (7.85); S11.97 (11.98).

Antibacterial Studies

The antibacterial activity of the compound, $(HAAP^+.HTBA^-)$ was evaluated by means of Disc Diffusion[15,16] method against B.Cerus, V.Cholerae, S.Typhimurium and S. Aureaus and the results were discussed in the **table 4**.

Non-linear optical properties of $(HAAP^+.HTBA^-)$ and $(HAAP^+)_2[Mg(TBA)_2]^{2-}$

The proton transfer salt, $(HAAP^+.HTBA^-)$ and $(HAAP^+)_2[Ni(TBA)_2]^{2-}$ were subjected to SHG measurement and the results are presented in **Table 5**. From the powder SHG measurement, it is clear