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3-(2-BENZOTHIAZOLYLAZO)THENOYLTRIFLUORO ACETONE AND ITS Cu(II), Co(II), Ni(II) AND Zn(II) COMPLEXES

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ABSTRACT

The coupling of diazotized 2-aminobenzothiazole with thenoyltrifluoroacetone resulted in the formation of a tridentate ligand (HL). Azo-enol tautomeric form of the compound with intramolecular hydrogen bond is confirmed by spectral and analytical data. Formation of its [CoL_2], [NiL_2], [CuL(OAc)] and [ZnL_2] complexes with monobasic tridentate coordination is also proposed based on analytical and spectral data. Magnetic studies revealed that Cu(II), Ni(II) and Co(II) complexes are paramagnetic while the Zn(II) chelate is diamagnetic.

Keywords: Benzothiazolylazo Derivative, Thenoyltrifluoroacetone, Azo-enol Form, Metal Complexes, Spectral Studies.

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INTRODUCTION

Thenoyltrifluoroacetone is a β-diketone and an inhibitor of cellular respiration.[1,2] Studies indicate that it inhibits carboxylesterase and mitochondrial complex II activities.[2,3] It has been investigated as a better complexing agent than acetylacetone for the separation and purification of various metal ions[3]. Diazo coupling of aryldiazonium ion with 1,3-dicarbonyls is used for preparing many important fabric dyes and pigments.[4,5] In heteroarylazo derivatives of β-diketones, the heteroatom can donate electron pair to metal cation due to proximity effects.[6-8] Literature is extensive on the structural aspects of complexes of azo-β-diketones and allied compounds.[6-14] However, reports are scanty on heteroarylazo derivatives of thenoyltrifluoroacetone. As a part of our interest in the study of heteroarylazo derivatives of 1,3-dicarbonyl compounds and their metal complexes, the present report communicates the synthesis and characterization of a new type of tridentate azodye obtained by coupling diazotized 2-aminobenzothiazole with thenoyltrifluoroacetone.[6-8,14] Co(II), Ni(II), Cu(II) and Zn(II) complexes of this ligand are also synthesized and characterized.

EXPERIMENTAL

Material and Methods

The elemental analysis was done by microanalyses (Heraeus Elemental analyzer) and AAS (Perkin Elmer 2380 spectrometer). The electronic spectra of the compounds in methanol (10^{-4} mol/L) were recorded on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, ^{1}H NMR spectra ($CDCl_3$ or DMSO-d_6) on a Varian 300 NMR spectrometer and mass spectra on a Jeol/SX-102 mass spectrometer (FAB using argon and *meta*-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF (~10^{-3} mol/L) at room temperature. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance at room temperature using $Hg[Co(NCS)_4]$ as the standard. 2-Aminobenzothiazole, thenoyltrifluoroacetone, methanol, urea and metal acetates used were of AR grade.

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Preparation of 3-(2-benzothiazolylazo)thenoyltrifluoroacetone (HL)

An aqueous solution of benzothiazole-2-diazonium ion was synthesized.[15] After destroying the excess nitrous acid with urea, the diazonium salt solution (0.01 mol) was added slowly with stirring to an ice-cold solution of thenoyltrifluoroacetone (0.01 mol in 25 mL ethanol). Cold NaOH solution (1 M, 20 mL) was added dropwise to maintain the pH of the mixture around 5. After continuous stirring of about half an hour, the precipitated compound was filtered and washed several times with deionized water till the co-precipitated sodium sulphate was completely removed. The crude product was recrystallized twice from hot benzene to get chromatographically pure material (TLC on silica gel, the solvent was acetone). The compound was crystalline and is soluble in common organic solvents.

Synthesis of Ni(II), Co(II), Cu(II) and Zn(II) Complexes

To a solution of the ligand (0.02 mol in 20 mL methanol) a concentrated aqueous solution of metal(II) acetate (0.01 mol) was added and stirred for ~2 h. The precipitated complex was filtered, washed with water, recrystallized from hot chloroform and dried in a vacuum.

RESULTS AND DISCUSSION

The elemental analytical data indicate 1:1 ratio for the diazo coupled product (HL) of diazotized 2-aminobenzothiazole and thenoyltrifluoroacetone (Fig.-1). [ML_2] stoichiometry of the Co(II), Ni(II) and Zn(II) complexes (Fig.-2) is evident from the analytical data (Table-1) and their non-electrolytic nature in DMF solvent (specific conductance <10 $\Omega^{-1}cm^{-1}$; 10^{-3} M solution). Cu(II) complex has [CuL(OAc)] stoichiometry (Fig.-3). The Zn(II) chelate is diamagnetic, as expected, while all other complexes showed paramagnetic moments within the range.

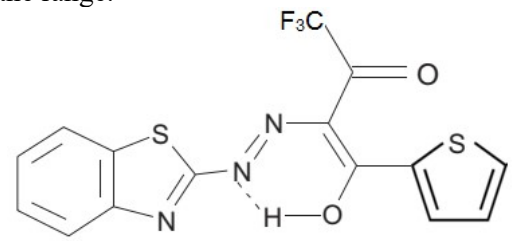

Fig.-1: The Proposed Structural Formula of HL

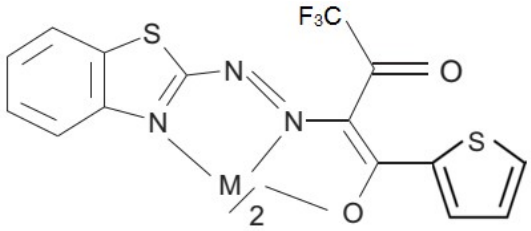

Fig.-2: The Proposed Structural Formula of the Metal Complexesof HL; M = Co(II), Ni(II) and Zn(II)

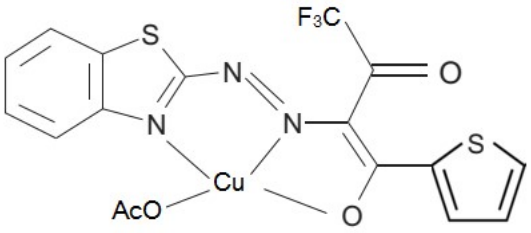

Fig.-3: The Proposed Structural Formula of the Cu(II) Complex of HL

IR Spectra

The free carbonyl band of the trifluoroacetyl group of HL appears at 1705 cm^{-1}.[13,16,17] The observed free carbonyl stretching frequency strongly supports the fact that the free carbonyl group in unsymmetrical 1,3-dicarbonyls is the one in which the carbonyl oxygen is less electron-rich. The strong band observed at

1640 cm^{-1} is due to the stretching of the enolised carbonylgroup.[14] C–O–H in-plane bending and ν(N=N) are observed at 1280 and 1455 cm^{-1} respectively as two medium intensity bands.[16,17] The ν(C=N) of benzothiazole ring is observed at 1620 cm^{-1} and ν(C=C) of the aryl ring appeared at 1580 cm^{-1}. The broad band in the range 2500-3500 cm^{-1} confirms strong intramolecular hydrogen bonding in the compound. Thus the IR spectrum of HL supports the intramolecular hydrogen-bonded azo-enol tautomeric form of the compound as in Fig.-1.

Table-1: Physical and Analytical data of HL and its Metal Complexes

Compound/ Empirical formula	Yield%	M.P. ^0C	Elemental Analysis:Found (Calculated)%			
			C	H	N	M
$HLC_{15}H_8F_3N_3S_2O_2$	55	135	46.60 (46.90)	2.15 (2.00)	10.50 (10.90)	-
[CuL(OAc)] $C_{17}H_{10}CuF_3N_3S_2O_4$	65	225	39.85 (40.43)	1.82 (1.98)	8.90 (8.32)	12.01 (12.59)
$[CoL_2]$ $C_{30}H_{14}CoN_6F_6S_4O_4$	70	210	42.75 (43.74)	1.65 (1.70)	11.20 (10.20)	6.90 (7.16)
$[NiL_2]$ $C_{30}H_{14}N_6NiF_6S_4O_4$	65	200	43.20 (43.75)	1.52 (1.70)	10.81 (10.21)	6.52 (7.14)
$[ZnL_2]$ $C_{30}H_{14}N_6F_6S_4ZnO_4$	75	205	43.10 (43.40)	1.72 (1.69)	9.70 (10.13)	7.15 (7.89)

In the IR spectra of all the metal complexes, the free carbonyl band of the ligand is only slightly shifted. This indicates that the free carbonyl group is not involved in metal coordination. The band due to the hydrogen-bonded carbonyl group of the ligand vanishes and a new band appeared at ~1570 cm^{-1} supporting the involvement of the enolised carbonyl group in bonding with the metal ion.[18] The free ligand band observed at 1280 cm^{-1} due to C–O–H bending and the broad free ligand band in the region 2500-3500 cm^{-1} disappeared in the spectra of all the metal complexes. Both these factors strongly support the replacement of enol proton of the ligand by metal ion during complex formation.[6,7,18] Several medium intensity bands are observed in the 2500-3500 cm^{-1} region of the spectra assignable to various ν(C-H) vibrations. In the spectra of the complexes, the bands due to ν(N=N) and benzothiazole ν(C=N) of the ligand shifted appreciably to lower wave numbers indicating the coordination of these groups in bonding with the metal ion as in Fig.-2 and Fig.-3 (Table-2).

IR spectrum of the Cu(II) complex showed a comparatively strong band at 1625 cm^{-1} and a medium intensity band at 1310 cm^{-1} due to the antisymmetric and symmetric stretching of monodentate acetate group respectively as in Fig.-3.[6,7,18] The appearance of new medium intensity bands in the 420-480 and 530-580 cm^{-1} region of the spectra due to ν(M–O) and ν(M–N) also support Fig.-2 and Fig.-3.[18]

Table-2: Characteristic IR Stretching Bands (cm^{-1}) of HL and its Metal Complexes

Compound	Free(C=O)	Chelated (C=O)	(C=N)	(N=N)	(M–N)	(M–O)
HL	1705	1640	1620	1455	-	-
[CuL(OAc)]	1705	1570	1598	1435	538	432, 472
$[CoL_2]$	1710	1568	1590	1433	547	412, 476
$[NiL_2]$	1710	1572	1594	1430	545	425, 475
$[ZnL_2]$	1708	1566	1586	1428	578	420, 478

^{1}H NMR Spectra

The intramolecular hydrogen-bonded enol proton of HL appeared as a low field one proton signal at δ 14.10 ppm.[6,7,19] This signal disappeared in the ^{1}H NMR spectrum of the diamagnetic Zn(II) complex, indicating the replacement of enol proton by metal ion during chelate formation.[6,7] The aryl protons appeared like a complex multiplet in the range δ 6.8 to 8.1 ppm.

Mass Spectra

The presence of an intense molecular ion peak at m/z 383 in the mass spectrum of HL confirms the formulation of the compound as in Fig.-1. The azo structure of the compound is evident from the presence of the peak due to the elimination of ArN_2 from molecular ion.[7,20] Fragments due to the elimination of

CF_3CO and C_4H_3SCO are also present in the spectrum. The observed peak at *m/z* 175 is due to the ion radical through the elimination of CF_3CO and C_4H_3SCO from P^+. This peak also rules out the existence of the compound in the hydrazone form because in such case the most facile reaction will be the cleavage of N-N bond[8,21]. Thus the peaks observed in the spectrum strongly support the existence of the compound in the azo-enol form rather than in the keto-hydrazone form.

[CuL(OAc)] and [NiL_2] stoichiometry of the Cu(II) and Ni(II) complexes are revealed from the presence of corresponding molecular ion peaks in their FAB mass spectra. Peaks due to $[P - CF_3CO]^+$, $[P - C_4H_3SCO]^+$, $[C_4H_3SCO]^+$, $[CF_3CO]^+$, $[ML]^+$, L^+ and fragments of L^+ are present in the spectra. The peaks due to the removal of the acetate group and several fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes are also present in the mass spectrum of the Cu(II) complex. The important mass spectral fragments are tabulated in Table-3.

Table-3: Mass Spectral Data of HL and its Cu(II) and Ni(II) Complexes

Compound	Mass Spectral Data (m/z)
HL	383, 286, 272, 221, 175, 111, 97
[CuL(OAc)]	506, 504, 409, 407, 447, 445, 395, 393, 383, 336, 334, 298, 296, 286, 239, 237, 175, 111, 97
[NiL_2]	823, 726, 712, 629, 615, 601, 518, 441, 407, 383, 175, 111, 97

Electronic Spectra

Various n→π* and π→π* transitions are confirmed by two broad bands with maxima at 380 nm and 270 nm in the UV spectrum of HL. In the spectra of metal complexes, these values shifted slightly to a longer wavelength indicating the involvement of carbonyl and azo groups in metal complexation.[12]

Cu(II) complex displayed a broad visible band at 15,000 cm^{-1}. This, along with the measured μ_{eff} value (1.75 B.M.), supports its square-planar structure.[22] The Ni(II) chelate shows three well-separated absorption bands in the spectrum at λ_{max} 8,200, 13,100 and 24,300 cm^{-1} corresponding to the transitions; $^3A_{2g}\rightarrow{}^3T_{2g}$; $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ respectively.[6] These, together with their measured μ_{eff} value (2.80 BM), support the octahedral structure of the complex. The spectrum of the Co(II) complex showed three bands at λ_{max} 9,500, 12,000 and 20,000 cm^{-1} corresponding to the transitions $^4T_{1g}(F)\rightarrow{}^4T_{2g}$; $^4T_{1g}(F)\rightarrow{}^4A_{2g}$; $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$, respectively. The transition to $^4A_{2g}$ is very weak and appears as a shoulder. This, together with the measured μ_{eff} value (4.82 BM.), suggest its octahedral geometry.[23]

CONCLUSION

A new arylazo derivative (HL) is prepared by coupling benzothiazole-2-diazonium ion with the active methylene group of thenoyltrifluoroacetone. Analytical and spectral data confirmed its existence in the azo-enol tautomeric form in which the carbonyl group bearing the benzothiazole group has enolized and hydrogen-bonded to one of the azo nitrogen, and the carbonyl group of trifluoroacetyl group remained in the keto form. Monobasic tridentate coordination of the compound involving cyclic nitrogen, one of the azo nitrogen and the enolate oxygen has been confirmed from the analytical and spectral data of the metal chelates. The Cu(II) complex conforms to [CuL(OAc)] stoichiometry while Co(II), Ni(II) and Zn(II) complexes are in agreement with [ML_2] stoichiometry.

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