



Trade Science Inc.

June 2009

Volume 4 Issue 2

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 4(2), 2009 [83-87]

3-(2-Pyridylazo)-2,4-pentanedione and its metal chelates

Krishnannair Krishnankutty¹, Muhammed Basheer Ummathur^{2*}, Damodaran Kamalakshy Babu³

¹Department of Chemistry, University of Calicut, Kerala-673635, (INDIA)

²Department of Chemistry, Unity Women's College, Manjeri, Kerala-676122, (INDIA)

³Department of Chemistry, Zamorin's Guruvayurappan College, Calicut, Kerala-673014, (INDIA)

E-mail : mbummathur@rediffmail.com

Received: 18th March, 2009 ; Accepted: 23rd March, 2009

ABSTRACT

The coupling of diazotised 2-aminopyridine with acetylacetone yielded a new type of tridentate ligand. Analytical, IR, ¹H NMR, ¹³C NMR and mass spectral data indicate the existence of the compound in the intramolecularly hydrogen bonded azo-enol tautomeric form. Monobasic tridentate coordination of the compound in its [CuL(OAc)] and [ML₂] complexes [M = Ni(II), Zn(II) and Pd(II)] has been established on the basis of analytical and spectral data. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Pyridylazoacetylacetone;
Azo-enol form;
Metal complexes;
IR spectra;
¹H NMR spectra;
Mass spectra.

1. INTRODUCTION

Metal dye complexes play a very important role in dyestuff technology^[1] and find application in many other fields, especially in analytical chemistry^[2]. The metal ions alter the properties of the dye, both qualitatively and quantitatively^[3]. Complexes derived from tridentate azo compounds represent the single most important class of metal complex dyestuffs. In recent years significant number of tridentate azo compounds containing heteroaryl ring systems have been developed in order to improve the colouring properties, and to achieve more specificity and selectivity in chemical analysis^[4]. However metal complexes of these dyestuffs do not received as much attention as they deserve. In continuation of our studies on arylazo derivatives of 1,3-diketones and their metal complexes^[5-11], we report herein the synthesis and characterization of a new type of tridentate azodye obtained by coupling diazotized 2-aminopyridine

with acetylacetone. Typical metal complexes of the compound were also synthesized and characterized.

2. EXPERIMENTAL

2.1. Materials and methods

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The IR spectra (KBr discs) were recorded on a 8101 Shimadzu FTIR spectrophotometer, ¹H NMR spectra in CDCl₃ or DMSO-d₆ 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 at 28±1°C using solution of about 10⁻³ M concentration. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

Full Paper

TABLE 1: Physical and analytical data of Hpaac and its metal complexes

Compound/Empirical formula	Yield %	m.p. °C	Elemental analysis: Found (Calculated)%			
			C	H	N	M
Hpaac C ₁₀ H ₁₁ N ₃ O ₂	75	99	58.40(58.54)	5.40(5.37)	20.55(20.49)	-
[Ni(paa) ₂] C ₂₀ H ₂₀ N ₆ NiO ₄	65	202	51.46(51.42)	4.33(4.28)	18.03(18.00)	12.65(12.58)
[Cu(paa)(OAc)] C ₁₂ H ₁₃ CuN ₃ O ₄	65	286	44.20(44.10)	3.90(3.98)	12.95(12.86)	19.54(19.46)
[Zn(paa) ₂] C ₂₀ H ₂₀ N ₆ O ₄ Zn	70	240	50.78(50.70)	4.28(4.22)	17.60(17.74)	13.75(13.81)
[Pd(paa) ₂] C ₂₀ H ₂₀ N ₆ PdO ₄	70	238	46.56(46.66)	3.83(3.89)	16.43(16.33)	20.75(20.65)

2.2. Synthesis of pyridylazoacetylacetone, Hpaac

An aqueous solution of pyridine-2-diazonium ion was prepared by standard method^[12] After destroying the excess nitrous acid with urea, the solution (0.01 mol) was added drop by drop with stirring to an ice-cold (< 5°C) solution of acetylacetone (0.01 mol, 20 mL absolute ethanol). The pale red solution so formed was kept for 15 days. The pale yellow crystals formed during this time were then filtered, washed with water and recrystallized twice from hot methanol to get chromatographically (TLC) pure compound.

2.3. Synthesis of Ni(II), Cu(II), Zn(II) and Pd(II) complexes

To a methanolic solution of the ligand (0.02 mol, 30 mL) a concentrated aqueous solution of metal(II) acetate (0.01 mol) in minimum amount of water was added and stirred for ~2 h on a magnetic stirrer. The precipitated complex was filtered, washed with water and recrystallized from hot chloroform to get chromatographically (TLC) pure compound.

3. RESULTS AND DISCUSSION

The observed elemental analytical data of the pyridylazoacetylacetone indicate that diazo-coupling reaction has occurred in the 1:1 ratio (TABLE 1). The compound is crystalline in nature and is soluble in common organic solvents. It formed stable complexes with Ni(II), Cu(II), Zn(II) and Pd(II) ions. The analytical data (TABLE 1) together with non-electrolytic nature in DMF (specific conductance $10\Omega^{-1}\text{cm}^{-1}$; 10^{-3} M solution) suggest [ML₂] stoichiometry of the complexes except for the Cu(II) complex which has [CuL(OAc)] stoichiometry. The Zn(II) and Pd(II) chelates are diamagnetic while Ni(II) and Cu(II) complexes showed normal paramagnetic moment. The observed IR, ¹H NMR, ¹³C NMR and mass spectral data are in conformity with figure 1 of the pyridylazoacetylacetone and

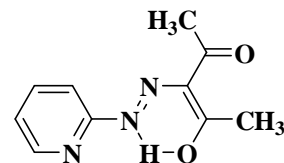


Figure 1: Structure of Hpaac

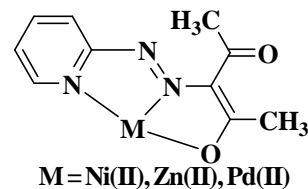


Figure 2 : Structure of the metal complexes of Hpaac

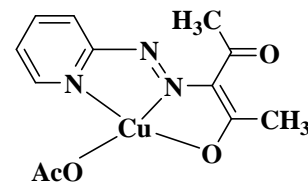


Figure 3. Structure of the Cu(II) complex of Hpaac

figure 2 of the complexes. The Cu(II) complex conform to figure 3.

3.1. Infrared spectra

The IR spectrum of Hpaac in the region 1600-1800 cm⁻¹ show two strong peaks at 1680 and 1639 cm⁻¹ assignable respectively to the stretching of free conjugated and enolised acetyl carbonyl groups^[13] of figure 1. In the spectrum of the compound two medium intensity bands are observed at 1280 and 1440 cm⁻¹ assignable to C–O–H in-plane bending and νN=N respectively^[14,15]. The aromatic νC=C vibrations appeared at ~1580 cm⁻¹ and pyridine ring νC=N is observed at 1610 cm⁻¹. Spectrum of the compound showed a broad band ranging from 2350 to 3500 cm⁻¹ due to strong O–H...N hydrogen bonding. The presence of two strong bands at 995 and 710 cm⁻¹ is indicative of the presence of

TABLE 2: Characteristic IR stretching bands (cm^{-1}) of Hpaa and its metal complexes

Compound	Free (C=O)	Chelated (C=O)	(C=N)	(N=N)	(M-N)	(M-O)
Hpaa	1680 s	1639 s	1610 m	1440 m	-	-
[Ni(paa) ₂]	1685 s	1542 s	1582 m	1410 m	545 m	418 m
[Cu(paa)(OAc)]	1682 s, 1626 s, 1312 m	1540 s	1580 m	1413 m	542 m	422 m
[Zn(paa) ₂]	1680 s	1542 s	1584 m	1410 m	546 m	420 m
[Pd(paa) ₂]	1684 s	1548 s	1582 m	1412 m	540 m	424 m

In the case of copper complex two additional bands given under C=O are due to acetate group

TABLE 3: ¹H NMR spectral data (δ , ppm) of Hpaa and its Zn(II) and Pd(II) complexes

Compound	OH	Pyridyl	CH ₃
Hpaa	14.12(1H, s)	7.25–8.15(4H, m)	2.48 (3H, s) 2.61 (3H, s)
[Zn(paa) ₂]	-	7.18–8.05(8H, m)	2.52 (6H, s) 2.65 (6H, s)
[Pd(paa) ₂]	-	7.16–8.08(8H, m)	2.54 (6H, s) 2.69 (6H, s)

m = multiplet, s = singlet

TABLE 4: ¹³C NMR spectral data (δ , ppm) of Hpaa and its Zn(II) complex

Compound	C=O	CH ₃	C-N	Pyridyl
Hpaa	197.587	31.737	154.635	138.463
	196.284	26.515	148.472	133.894
				120.516
[Zn(paa) ₂]	195.611	33.413	160.077	109.250
	194.836	28.017	144.947	140.841
				133.276
				121.673
				110.752

pyridine ring^[15]. Thus the IR spectrum strongly support the existence of the compound in the intramolecularly hydrogen bonded azo-enol tautomeric form.

In the IR spectra of all the complexes the broad free ligand band in the region 2350–3500 cm^{-1} disappeared indicating the replacement of the enol proton by metal ion during complexation^[16]. Several medium intensity bands are present in the region of the spectra due to various $\nu\text{C-H}$ vibrations. The absence of the free ligand band at 1280 cm^{-1} due to C–O–H bending also supports the replacement of the enol proton by metal ion. The free conjugated acetyl carbonyl band of Hpaa is only marginally shifted indicating its non-involvement in coordination. However the band due to the hydrogen bonded carbonyl group disappeared and instead a new band appeared at $\sim 1550 \text{ cm}^{-1}$ in the spectra of all the complexes supporting the involvement of the enolised carbonyl in bonding with the metal ion. In the spectra of all the complexes, the band at 1440 cm^{-1} due to $\nu\text{N=N}$ and the band due to ring $\nu\text{C=N}$ (1610

cm^{-1}) of the free ligand shifted appreciably to low wave number ($\sim 20\text{--}30 \text{ cm}^{-1}$) indicating the involvement of these groups in bonding with the metal ion as in figure 2. In the IR spectrum of the Cu(II) complex a comparatively strong band at 1626 cm^{-1} and a medium intensity band at 1312 cm^{-1} appeared due to antisymmetric and symmetric stretching of monodentate acetate group^[17] as in figure 3. The presence of new medium intensity bands at ~ 420 and 540 cm^{-1} assignable to $\nu\text{M-O}$ and $\nu\text{M-N}$ in the spectra of all the complexes^[17] also support figures 2 and 3. Important bands that appeared in the spectra are given in TABLE 2.

3.2. NMR spectra

The ¹H NMR spectrum of Hpaa is characterized by the presence of a low field one proton signal at δ 14.12 ppm which is considerably lower than that reported for arylazo derivatives of 1,3-diketones that exist in the hydrazone form^[5–9]. Since azo-enol protons show signal in the range δ 10–14 ppm, the signal at δ 14.12 ppm can be assigned to the intramolecularly hydrogen bonded enol proton^[5,11,18]. The spectrum showed two methyl proton signals of equal intensity at δ 2.48 and 2.61 ppm indicating that the two are in different electronic environments. The aryl protons are observed in the range δ 7.25–8.15 ppm as a complex multiplet. In the ¹H NMR spectra of the diamagnetic Zn(II) and Pd(II) complexes, the low field signal due to the intramolecularly hydrogen bonded OH proton disappeared indicating its replacement by metal cation during complexation^[19]. The integrated intensities of various signals agree well with the [ML₂] stoichiometry of the complexes (TABLE 3).

The ¹³C NMR spectrum of Hpaa clearly indicates its existence in the azo-enol form. That the two carbonyl groups are in different electronic environment is evident from the large separation of the carbonyl carbon signals. The involvement of the enolate oxygen and

Full Paper

TABLE 5: Mass spectral data of Hpaa and its Ni(II) and Cu(II) complexes

Compound	Mass spectral data (m/z)
Hpaa	205, 177, 162, 119, 106, 99
[Cu(paa) (OAc)]	328, 326, 285, 283, 269, 267, 250, 248, 226, 224, 207, 205, 162, 119, 106, 99
[Ni(paa) ₂]	467, 424, 389, 381, 346, 311, 303, 268, 263, 225, 205, 177, 162, 119, 106, 99

hetero nitrogen atom in bonding with the metal ion is evident from the positions of the various signals^[11] in the ¹³C NMR spectrum of its Zn(II) complex (TABLE 4).

3.3. Mass spectra

The formulation of the compound as in figure 1 is clearly supported from the presence of intense molecular ion peak in the mass spectrum at *m/z* 205. Presence of peak at *m/z* 99 due to the elimination of ArN₂ from molecular ion, characteristic of tautomers^[20,21], in the spectrum support the azo structure. Fragments due to the elimination of CH₃CO, pyridine group, etc. are typical of the spectrum. The origin of the peak at *m/z* 119 of Hpaa can be explained by the formation of the ion radical Py-N₂CH⁺ (Py = pyridine ring) through the elimination of both CH₃CO groups from P⁺. Had the compound existed in the hydrazone form, the most facile reaction involves the cleavage of N-N bond^[21] and the ion of *m/z* 119 would not have originated. Thus the mass spectrum supports the existence of the compound in the azo-enol form rather than the keto-hydrazone form. The FAB mass spectra of the Cu(II) and Ni(II) complexes showed molecular ion peaks corresponding to [CuL(OAc)] and [NiL₂] stoichiometries. Peaks correspond to [P - CH₃CO]⁺, [CH₃CO]⁺, [ML]⁺, L⁺ and fragments of L⁺ are also present in the spectra. The spectrum of the Cu(II) complex also showed peaks due to [P - CH₃COO]⁺ and a number of fragments containing copper in the 3:1 natural abundance of ⁶³Cu and ⁶⁵Cu isotopes (TABLE 5).

3.4. Electronic spectra

The UV spectrum of Hpaa showed two broad bands with maxima at 380 nm and 250 nm due to various n→π* and π→π* transitions. In complexes these absorption maxima shifted appreciably to low wave numbers. The Cu(II) complex showed a broad band centered at 15,200 cm⁻¹. This, together with the measured μ_{eff} value (1.74 BM) suggests the square-planar geom-

etry^[22]. The Ni(II) chelate is paramagnetic (μ_{eff} value 2.80 BM) and show three well-separated absorption bands in the spectrum at λ_{max} 8,100, 13,300 and 24,400 cm⁻¹ corresponding to the transitions; ³A_{2g} → ³T_{2g}, ³A_{2g} → ³T_{1g}(F) and ³A_{2g} → ³T_{1g}(P) respectively. So the metal ion will be in an octahedral environment.

4. CONCLUSIONS

Pyridylazoacetylacetone has been prepared by the coupling of diazotized 2-aminopyridine with acetyl acetone. Analytical, IR, ¹H NMR, ¹³C NMR and mass spectral data revealed a 1:1 product in which one of the carbonyl group of the diketone is enolized and involved in intramolecular hydrogen bonding with one of the azo nitrogens. Analytical, physical and spectral data of the [ML₂] complexes of Ni(II), Zn(II) and Pd(II) showed the monobasic tridentate N₂O coordination involving one of the azo nitrogen, ring nitrogen and enolized carbonyl oxygen. The Cu(II) complex conform to [CuL(OAc)] stoichiometry.

5. REFERENCES

- [1] K.Venkataraman; 'Chemistry of Synthetic Dyes', Academic Press, New York, **5**, (1977).
- [2] R.R.Myers, J.L.Long; 'Pigments', Part I, Marcel Dekker; New York, (1975).
- [3] O.G.Khudina, Y.V.Burgart, N.V.Murashova, V.I. Saloutin; Russian J.Org.Chem.**39**, 1421 (2003).
- [4] T.Yasui, N.Komatsu, K.Egami, H.Yamada, A. Yuchi.; Anal.Sci., **23**, 1011 (2007); M.G.B.Drew, B.Vickery, G.R.Willey; J.Chem.Soc., Perkin Trans., II, **10**, 1297 (1982).
- [5] K.Krishnankutty, P.Sayudevi, M.B.Ummathur; J.Indian Chem.Soc., **84**, 518 (2007).
- [6] K.Krishnankutty, V.T.Reman; Synth.React.Inorg. Met.Org.Chem., **25**, 243 (1995).
- [7] K.Krishnankutty, J.Michael; J.Indian Chem.Soc., **70**, 238 (1993); J.Coord.Chem., **24**, 259 (1993); J.Coord.Chem., **22**, 327 (1991).
- [8] K.Krishnankutty, P.Ummathur; J.Indian Chem.Soc., **66**, 194 (1989); J.Indian Chem.Soc., **65**, 213 (1988).
- [9] N.Thankarajan, K.Krishnankutty; Indian J.Chem., **23A**, 401 (1984).
- [10] K.Krishnankutty, P.Sayudevi, M.B.Ummathur; J.Indian Chem.Soc., **85**, 48 (2008); J.Indian

- Chem.Soc., **84**, 337 (2007); J.Serb.Chem.Soc., **72**, 1075 (2007).
- [11] K.Krishnankutty, D.K.Babu; J.Indian Chem.Soc., **73**, 379 (1996).
- [12] R.C.Elderfield; 'Heterocyclic compounds', John Wiley; New York, **1**, (1950).
- [13] K.Krishnankutty, M.B.Ummathur; J.Indian Chem.Soc., **83**, 639 (2006); K.Nakamoto, H.Ogoshi; J.Chem.Phys., **45**, 3113 (1966).
- [14] L.J.Bellamy; 'The Infrared Spectra of Complex Molecules', Chapman and Hall, London, (1980).
- [15] C.N.R.Rao; 'Chemical Applications of Infrared Spectroscopy', Academic Press; London, (1963).
- [16] V.D.John, K.Krishnankutty; Appl.Organometal. Chem., **20**, 477 (2006).
- [17] N.Nakamoto; 'Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds', John Wiley & Sons; New York, (1997).
- [18] A.Lycka, J.Jirman, A.Cee; Magnetic Res.Chem., **28**, 408 (1990).
- [19] D.C.Nonhebel; Tetrahedron, **24**, 1869 (1968).
- [20] H.Budzikiewicz, C.Djerassi, D.H.Williams; 'Mass spectrometry of organic compounds', Holden Day, San Francisco, (1967).
- [21] K.Kobayashi, K.Kurishara, K.Hirose; Bull.Chem. Soc.Jpn., **45**, 3551 (1972).
- [22] K.C.Joshi, V.N.Pathak; Coord.Chem.Rev., **22**, 37 (1977).