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Synthesis and the structural elucidation of 2-thio picolinamide (TPA) and 2-N-benzyl TPA

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ABSTRACT

The present work is concerned with the synthesis and the structural elucidation of the two ligands, viz., 2-thio picolinamide (TPA) and 2-N-benzyl TPA. The isolated solid complexes are subjected to characterised by Wet chemical analysis (N, S, metal), Conductivity measurements, Infrared including far infrared spectral measurements and H^1 NMR, and Mass spectral measurements.

Introduction

Coordination chemistry is one of the most active branches of inorganic chemistry. The coordination compounds find wide applications virtually in all branches of chemistry. Metal ions form a variety of complexes with a number of neutral and anionic ligands. The pioneering work of Werner and Jorgensen[1] led to an understanding of the properties of these complexes. Analytical chemists have devised methods for the detection, separation and estimation of metal ions based on their ability to form complexes selectively. Metal ions like iron, copper, manganese and zinc have been found to be essential for sustaining the life processes. It has been observed that these metal ions are required for the activity of enzymes, for the transport of oxygen and for many redox reactions, that are an essential part of biochemical processes. Some metal ion like iron, cobalt, zinc, molybdenum, copper and their chelates serve as micronutrients for plants. One of the most important problems in coordination chemistry has been the determination of the nature and the strength of the metal-ligand bond, structure and reactivity. The nature of the coordination compounds depends on a number of factors, such as the donor atom and its oxidation state, the structure of the ligand, the anion present and the mode of synthesis.

Preparation of the ligands

The two ligands TPA and 2-N-benzyl TPA were prepared by a one step process starting from the respective 2-cyanopyridine.

(i) Preparation of 2-thiopicolinamide (TPA) from 2-cyanopyridine: 2g of 2-cyanopyridine were dissolved in dilute alcoholic solution and 5ml of liquid ammonia solution were added to make the solution distinctly ammoniaccal. Dry hydrogen sulphide gas was bubbled at a slow rate through the solution from a Kipp's apparatus. The solution immediately turned yellow and after half-an-hour the solid started precipitating out. In about 2 hours time, the precipitation was complete. The contents were cooled sufficiently and filtered. The yellow solid residue was repeatedly washed with water to free it from any absorbed hydrogen sulphide gas and other soluble impurities. It was recrystalised from hot water, filtered and dried.

Colour : Yellow m.pt. : 135°C Yield : 2.1g

(ii) Preparation of 2-N-benzyl TPA from 2-cyanopyridine: 2g of 2-cyanopyridine were dissolved in dilute alcoholic solution and 10-15ml of benzylamine solution were added. Dry hydrogen sulphide gas was bubbled slowly through the solution as before. The yellow solid precipitated out only after one hour. It was filtered and washed repeatedly with water and recrystallised from hot water.

Colour: Yellow m.p.t: 338°C Yield : 2.39g

The synthesis data for the compounds (ligands) is given in Table 1.

Physical Measurements

1. Conductance measurements: Conductivity measurements for the complexes were carried out with the help of a Philips Conductivity Bridge, in DMF solutions at 10^{-3}m concentration of the complexes with a closed type conductivity cell. The cell constant of the cell was measured each time using standard kCl solution[1].

2. Infrared spectral measurements: A Perkin Elmer spectrophotometer ($4000-200 cm^{-1}$) and ($4000-100 cm^{-1}$) employed to record the infrared spectra. The solid complexes were pressed into pellets using spectroscopic grade KBr. The instrument was calibrated and the sensitivity tested using a polystyrene film as a standard.

3. H^1NMR spectra: Proton NMR spectra of the ligands were recorded on a 300 MHz. NMR spectrometer varian model instrument using tetramethylsilane (TMS) as an internal reference. Values of chemical strifts reported in the present study are in the 5 scale. The solvents employed were $CDCI_3$.

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4. Mass Spectra: Mass spectra were obtained using a MSSEPI D18 instrument.

Analytical data

The carbon, hydrogen nitrogen and sulphur contents of the two ligands are collected in Table 2.

The percentage composition of compounds TPA and 2-N-benzyl TPA, their colour and melting points are presented in Table 2. Their empirical formula were determined from elemental analysis data.

Infrared spectra

The infrared spectra of TPA and 2-N-benzyl TPA are given in Fig. l and 2. The main bands are tabulated in the Table 3.

In the case of TPA, the compound exhibits a sharp band at 3349.5cm^{-1} and a rather medium band at 3226.8 cm^{-1}. The former peak can be assigned to the asymmetric stretching mode of thiomidic NH2 and the latter to the symmetric stretching mode[5]. However, there is a broad peak around 3147.5 cm^{-1} which may be the intra-molecularly hydrogen bonded NH2 group[2-3].

The typical bands in the region of 3400-3150 cm^{-1} and 3053cm^{-1} correspond to the N-H and C-H stretching vibrations respectively. The bands around 1510-1600cm^{-1}, 632-668cm^{-1} and 448-498cm^{-1} are indicative of the ring vibrations, ring breathing, out of-plane and in-plane deformations of pyridine respectively. A composite band in the region of 15144 and 1581cm^{-1} arises from N-H and C-H deformations and C-N stretching vibrations. The C=S stretching vibrations occurs at 727 and 733cm^{-1}

A reliable assignment of the C=S stretching frequency in the spectra of the thiocarbonyl compounds is of special significance. The C=S stretching mode as a group frequency is poorly characterised, although the analogous C=0 stretching vibration as a group frequency is well established. This arises form the incidence of coupling of C=S stretching vibrations with other molecular vibrations[4]. This is especially so when the C=S moiety is attached to a strongly mesomeric atom such as nitrogen. This results in a lowering of the C=S bond order. The higher mass of sulphur and the lower C=S bond order shifts the C=S stretching vibrations to lower wave numbers, conductive to coupling with other vibrations. Despite increasing efforts in recent years, the assignment of the C=S stretching frequency still possess many problems.

The IR spectrum of 2-N-benzyl TPA exhibits a strong band at 3239.4 cm^{-1} and a very weak band in the form of a shoulder at 3401.5 cm^{-1}, attributed to H-bonded N-H and free N-H, respectively.

The absence of a band in the 2600-2500 cm^{-1} region[5] characteristic of the -SH group in the spectra of the above compounds, indicates that the compounds are in the thione resonance form, atleast in the solid state.

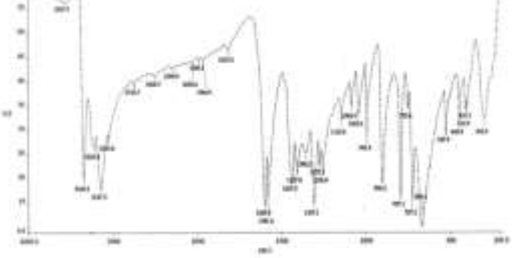


Fig. 1 - IR spectrum of TPA

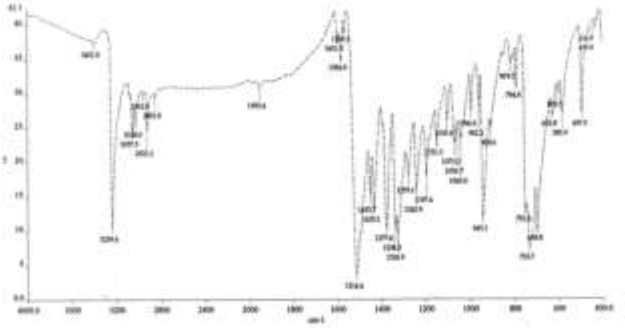


Fig. 2 - IR Spectrum of 2-N-benzyl TPA

H^{1} NMR spectra

The NMR (^{1}H) spectral data of TPA to 2-N-benzyl TPA (CDC1$_3$ solvent) are given in Table 4 and the spectra depicted in Figs 3 and 4. In the case of benzyl compounds (2-N-benzyl TPA peaks assignable to the benzylic and benzene ring protons are noticed around 5.0 and 7.4 δ respectively. The N-H protons (thioamidic) in 2-N-benzyl TPA are observed as a broad peak in the region 10.3 δ depending on the nature and position of the substituent present. The spectra TPA indicate the presence of peaks centered at about 8.5 δ, characteristic of the -NH$_2$ protons, while the N-H protons are expected to absorved further downfield (spectra recorded upto 10.3 δ only).

In general, 3 sets of peaks are observed for the pyridine ring protons for the 2-subsituted ligands (centered around 7.8, 7.3 and 8.4δ, expect the benzyl compound, exhibiting a peak further downfield at 8.7 δ) and 4 sets for the TPA ligands occurring at 7.4, 8.5, 8.7 and 9.5 δ as would be expected from considerations.

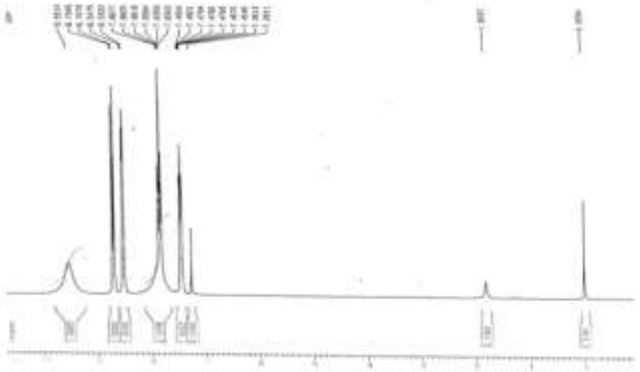


Fig. 3 - NMR spectrum of TPA

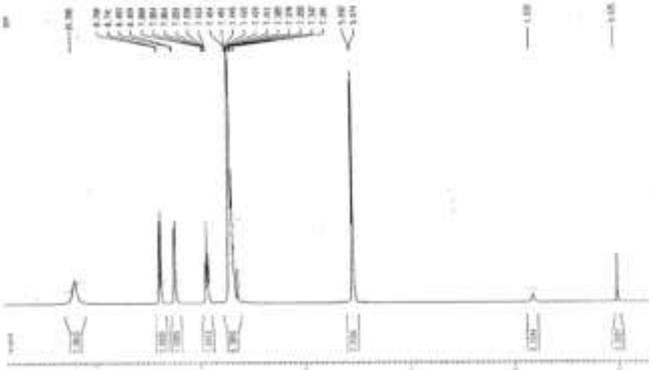


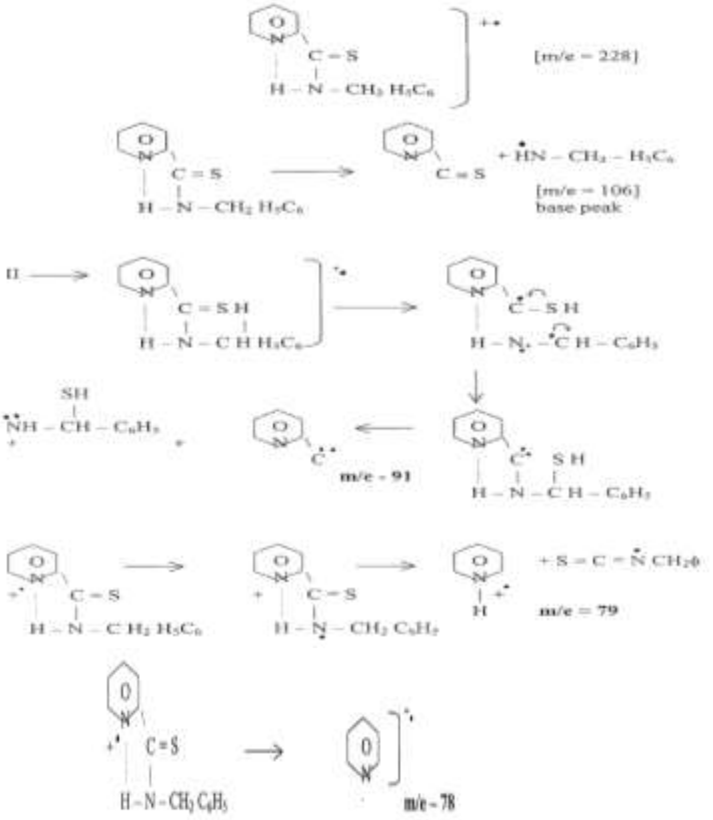
Fig. 4 - NMR Spectrum of 2-N-benzyl TPA

Mass spectra

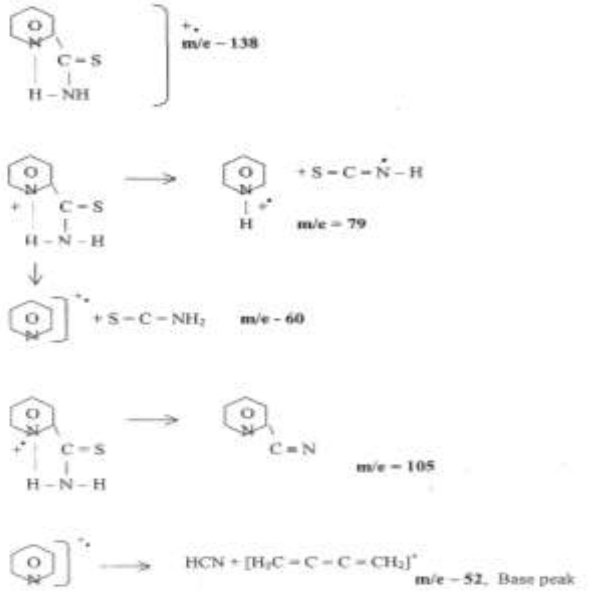
The mass spectra of the compound TPA and 2-N-benzyl TPA were recorded and the molecular weight was obtained from the molecular ion of the respective sample. The stability of the molecular ion is reflected in the molecular ion abundance. The spectra depicted in Figs. 5 and 6.

The mass spectrum of compound 2-N-benzyl TPA has an intense molecular ion peak (m/e=228) due to the stabilization of the positive charge by the π - electrons. Strongly peaks were observed at M-123, M-106, M-79 and M-51.

In the case of compound 2-N-benzyl TPA, the existence of intramolecular H-bonding, leading to a bicyclic like system, which could stabilize the positive charge better.



In the case of compound TPA molecular ion peak (m/e-138) is also the base peak in (m/e-52). Where as the base peak (m/e-52) is very intensity of the spectrum. Strong peaks were observed at M-79, M-60 and M-105.



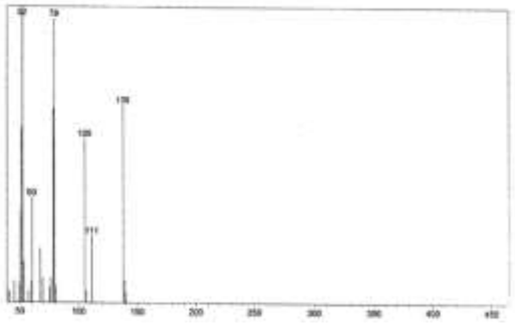


Fig. 5- Mass Spectrum of TPA

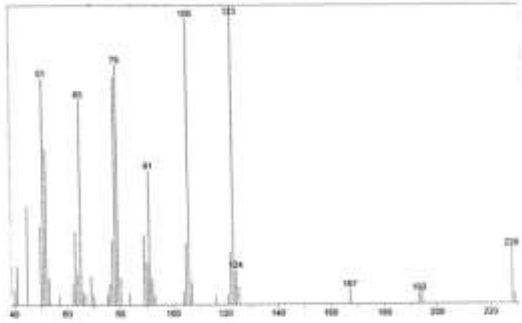
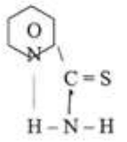
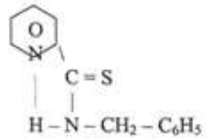


Fig. 6 - Mass spectrum of 2-N-benzyl TPA

Structure and coordination

The data given in section above indicate that the structure of the compounds prepared is of the following type





Of the compounds prepared and characterised TPA and 2-N-benzyl TPA were used as ligands in this study.

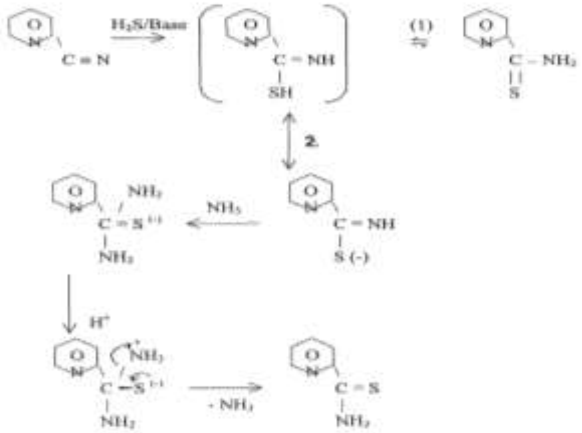
As the monodentate ligand, bonding via pyridine nitrogen, thiomidic nitrogen or thioamidic sulphur, ligation through the thioamidic nitrogen can occur as long as the delocalization is not disturbed due to coordination. This is possible when the ligand behaves as an anion. Owing to the loss of the thio amidic proton. Though postulated by some earlier workers[6] it has been disproved recently on the basis of x-ray structural studies[7].

As a bidentate ligand bonding through the thiocarbonyl sulphur and pyridine nitrogen atoms, resulting in a five – membered chelate[8].

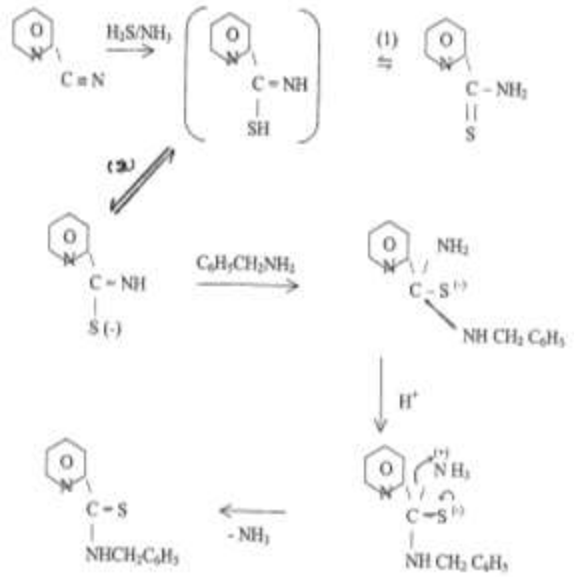
Formation of the ligand

Mechanism

Ligand – I (TPA)



Ligand – II (2-N-benzyl TPA)



Conclusion

The synthesis and the structural elucidation of the two ligands, viz., 2-thio picolinamide (TPA) and 2-N benzyl TPA were studied. The isolated solid complexes are subjected to various characterization by wet chemical analysis (N, S, metal), Conductivity measurements, Infrared including far infrared spectral measurements and H^1 NMR, and Mass spectral measurements.

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Table - 1
Characterisation of ligands

S.No.	Compound	Starting material	Colour	Yield	m.pt
1.	TPA	2-cyano pyridine	Yellow	2.1g	135°C
2.	N-benzyl-TPA	2-cyano pyridine	Yellow	2.3g	338°C

Table - 2
Elemental percentage composition data

*Mol. Wt.	m.p(k)	Ligand	% carbon		% hydrogen		% nitrogen		% sulphur		Mol. formula
			Expt	Calc	Expt	Calc	Expt	Calc	Expt	Calc	
138	135	I	15.17	14.9	4.34	4.09	20.28	19.7	23.18	22.8	$C_6H_6N_2S$
228	338	II	68.42	68.08	4.69	4.9	12.28	12.01	14.03	13.7	$C_{13}H_{12}N_2S$

* Value from the mass spectral data.

Table - 3
Characteristic IR frequencies (cm^{-1}) of the ligands

Compound		Assignment
I	II	
3349.5(s)	3239.4(s)	γ (N-H), asymmetric stretching
3226.8(m)	-	γ (NH), symmetric stretching
1581.4(m)	1584(s)	Pyridine ring vibrations
448.9(m)	497.5(m)	Pyridine ring vibrations (in-place)
668.4(m)	632.8(m)	Pyridine ring vibrations (out-of-plane)
727.2(s)	733.7(s)	γCS stretching
1600.9(s)	1514.4(s)	δ (NH) + γ (CN) + δ (CH) composite band I
1256(m)	1279.4(m)	γ (CN) + δ (NH) + δ (CH) + γ (CS) composite band II
3147.5(s)	-	γ NH Intra-molecular hydrogen bonded – NH_2 group

Abbreviations
(s): strong (m) : medium

Table - 4
^{1}H NMR data of the ligands for δ scale

Ligand No.		Type of protons
I	II	
-	7.4 (m)	$-C_6H_5$ protons
-	5.0 (d)	$-CH_2$ – (benzylic)
-	10.3 (s)	-NH – protons
7.8 (t of d)	-	$-NH_2$ protons
7.4 (t)	7.3 (m)	Pyridine ring protons
8.5 (d)	7.8 (t)	Pyridine ring protons
8.7 (d)	8.4 (d)	Pyridine ring protons
9.5 (s)	8.7 (d)	Pyridine ring protons

Abbreviations
s – Singlet d – doublet t – triplet m – multiplet