Characterisation of the complexes of Nickel II and Copper II of TPA and 2-N-benzyl TPA

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ABSTRACT

Nickel (II) complexes and Copper (II) complexes with the two ligands TPA and 2-N-benzyl TPA with nitrate anion are prepared. The isolated solid complexes are subjected to various physical measurements, such as conductivity measurements, and spectral behaviour apart from the chemical analysis.

Introduction

Ligands possessing more than one potential donor site but only one of which coordinates at a time are called ambidentate ligands[1], studies on ambidentate ligands have indicated that a number of factors such as the metal ion, its oxidation state, structure of the ligand, sterric effect, the ligands already present in the complex method of preparation, etc. influence their coordination behaviour and the change in the site of binding may be brought about by altering one or more of these factors. It may not always be possible to isolate the influence of one factor alone on the metal ligand bond.

Pearson[2] classified the metal ions and the donor atoms as hard and soft acids and bases considering the complexes as being formed by the interaction between a Lewis acid (metal ion) and a Lewis base (ligand). Evidences indicate that the bonds formed between the hard acid and hard base are predominantly ionic in character where as those formed by the combination of soft acid and soft base covalent in nature. Hard-hard, soft-soft interactions normally lead to stable complexes.

Metal ions exhibiting multiple valence state generally tend to behave soft in their lower oxidation states and hard in their higher oxidation states, eg. copper (I) exhibits soft acid character[3] towards a number of sulphur donor ligands while copper (II) shows hard acid character[4] with various sulphoxides. On the otherhand, Jorgensen[5] has pointed out that manganese shows soft character in high (+4 or +7) as well as low (+2) oxidation states and acts as a hard acceptor in (+2) state.

The present work is mainly concerned with the synthesis and the structural elucidation of 2-thio picolinamide (TPA) and 2-N-benzyl TPA using the above ligands, complexes of nickel (II) and copper (II) with nitrate anions. The isolated solid complexes are characterised by Wet chemical analysis (N, S, metal),Conductivity measurements, Infrared including far infrared spectral measurements and H[1] NMR, and Mass spectral measurements.

Preparation of the complexes

The solid complexes were prepared employing TPA and 2-N-benzyl TPA as ligands with nickel and copper in their divalent state in the from of their respective nitrates. The nitrates were taken as such.

(a) Preparation of nickel (II) complexes using TPA Using nickel (II) nitrate

1g of nickel (II) nitrate was dissolved in water and 2g of ligand solution in rectified spirit carefully mixed with constant stirring. The pH of the solution was adjusted to 8 by the addition of 1:1 ammonia solution in water. The precipitation of the complex was complete in about 30 minutes.
Colour of complex : Brown Yield : 0.7g

Preparation of nickel (II) complexes using 2-N-benzyl TPA Using nickel (II) nitrate : 1g of nickel (II) nitrate was dissolved in water and 2g of ligand solution in rectified spirit was carefully stirred with constant stirring. The pH of the solution was adjusted to 8 by the addition of 1:1 ammonia solution in water. The precipitation of the complex was complete in about 30 minutes.
Colour of complex : Brown Yield : 0:6g

Preparation of copper (II) complex using TPA Using copper (II) nitrate: 1g of copper (II) nitrate was dissolved in 10ml of carbonate free distilled water and 2g of the alcoholic solution of the ligand was carefully mixed with constant stirring. The solid complex formed almost instantaneously.
Colour of complex : Brown Yield : 0.8g

Preparation of copper (II) complex using 2-N-benzyl TPA Using copper (II) nitrate: 1g of copper (II) nitrate was dissolved in 10ml of carbonate free distilled water and 2g of the alcoholic solution of the ligand was carefully mixed with constant stirring. The solid complex formed almost instantaneously.
Colour of complex : Brown Yield : 0.6g

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Analytical techniques

(i) Estimation of nitrogen: Analysis of the nitrogen of the complexes was made using the micro kjeldahl technique with a Parnas wagner apparatus[6]. The general procedure is to convert the organic nitrogen to ammonia by digesting the compound with concentrated sulphuric acid in the presence of a suitable catalyst and estimating the ammonia formed by steam distilling it from the solution with strong alkali. The steam distilled ammonia is absorbed in a suitable acid and the amount of ammonia formed is volumetrically determined.

0.1 g of the complex was digested with 5ml of concentrated sulphuric acid in the presence of 0.5g of a 1:10 mixture of copper sulphate and potassium sulphate, the copper and potassium salts acting as catalysts in the conversion of organic nitrogen to ammonia. When the solution had become almost colourless (only a bluish tinge of copper salt was present), it was cooled and carefully made upto 50ml. A 10ml aliquot of this solution was transferred to the distillation flask of the Parnas wagner apparatus, 15ml, of a 50% solution of sodium hydroxide was added and the steam distillation started. The steam distilled ammonia was absorbed into a saturated solution of boric acid containing 2 drops of the mixed indicator consisting of methyl red and bromocresol green. The colour of the solution turned blue. It was titrated against a centinormal standard acid until the colour changed from blue to red. From the titre value, the percentage of nitrogen was calculated. The experiment was repeated for concordant values.

(ii) Estimation of sulphur: The complexes were decomposed with concentrated nitric acid containing a few ml of liquid bromine. Care was taken to effect complete oxidation of sulphur to sulphate and to minimise the possible decomposition of sulphuric acid by repeated treatment under controlled temperature with the oxidising agents. The sulphate was determined gravimetrically by precipitating and weighing as barium sulphate[7].

0.1g of the complex was weighted accurately and 10ml of concentrated nitric acid and 2ml of liquid bromine were added and the solution boiled to effect oxidation. The addition of nitric acid and bromine was repeated two or three times and the solution boiled well till the evolution of bromine vapours ceased. The solution was diluted to 100ml using distilled water and was heated to almost boiling. 5% barium chloride solution was added dropwise to the hot solution till the precipitation was complete. The precipitate was digested over a hot water bath for about an hour and the supernatant liquid was tested with barium chloride solution to ensure completion of precipitation. The contents were cooled well and the precipitate filtered through a whatman No.40 filter paper, first decanting the clear liquid and finally transferring the precipitate. The precipitate was repeatedly washed with hot water till drops of filtrate did not give a precipitate with silver nitrate solution. The filter paper was dried in an oven and the contents were in sinerated in a previously weighted silica crucible. From the difference in weights of the crucible, the amount of barium sulphate formed was found and hence the amount of sulphur present in the complex was calculated. The experiment was repeated for concordant values.

(iii) Estimation of nickel: The nickel content of the complexes was estimated by the volumetric back titration method using EDTA in the presence of Eriochrome Black T as indicator[8].

0.1g of the nickel complex was decomposed by digestion with concentrated sulphuric acid in the presence of perchloric acid. The digested solution was then made upto a known volume in a standard flask.

An aliquot of 5ml of the above solution was pipetted out and a slight excess of (10ml) of a standardised solution of EDTA was added. The solution was diluted to 50ml and 2ml of ammonia-ammonium chloride buffer solution was added to maintain the pH at 10. A few drops of Eriochrome Black-T indicator prepared in triethanolamine / alcohol solution were added and the solution was titrated against a standard zinc sulphate solution by direct titration. From the titre values, the amount of nickel present in the complex was calculated. The experiment was repeated for concordant values.

(iv) Estimation of copper: The copper content of the complexes was estimated by the volumetric titration method using sodium thiosulphate solution in the presence of starch as indicator.

0.1g of the copper complex was decomposed by digestion with concentrated sulphuric acid in the presence of perchloric acid. The digested solution was then mode upto a known volume in a standard flask.

An aliquot of 20ml of the above solution was pipetted out and slight excess of a ammonia solution was added and the solution was turned into deep blue colour. A few drops of acetic acid were added till the original blue colour was obtained. Then 20ml of 10% KI solution was added and the liberated iodine, then titrated against a standard sodium thiosulphate solution using starch indicator by direct titration. From the titre values, the amount of copper present in the complex was calculated. The experiment was repeated for concordant values.

Analytical data

The nitrogen, sulphur and metal contents of the various nickel (II) complexes are given in the Table 1.

When the elemental composition obtained experimentally is compared with the formulations proposed by calculation, the values agree with 1:2 mole ratio (metal : ligand) for all the two nickel (II) complexes.

The nitrogen, sulphur and metal contents of the various copper (II) complexes are given in Table 2.

When the elemental composition obtained experimentally is compared with the formulations proposed by calculation, the experimental values agree with 1:2 mole ratio (metal: ligand) for the complexes.

Infrared Spectra

The infrared spectra of the complexes were recorded in the 4000-200cm^{-1} region using KBr pellets. The composite mode due to δ_{CH}, δ_{NH} and ν_{CN} observed at 1598.3 cm^{-1} and 1542.9 cm^{-1} in the cse of I and II ligand respectively undergo a shift towards higher wave numbers as is evident from the Table 3. Clearly indicating sulphur coordination. Because of sulphur coordination, there is an increase in the C-N bond order and hence an increase. It is supported by the fact that the composite mode at 1242.1 cm^{-1} and 1284.9cm^{-1} in the respective ligand molecules undergo a downward shift to an extent of 20-60 cm^{-1} in the complexes towards lower wave numbers as is evident from the Tables. According to G.J. Sutton[9] which is further supported by weakening, complete disappearance or a negative shift of the band at 680 cm^{-1}.

The shift in the pyridine ring modes at 1649.5 cm^{-1}; 1014.9 cm^{-1} and 639cm^{-1} in ligand I complexes and the ligand II complexes 1545.4cm^{-1}; 1001 cm^{-1} and 502.7 cm^{-1} towards higher wave numbers, which is indicative of the pyridine nitrogen coordination.

The composite bands in the region of 1500-1550 cm^{-1} and 1230-1260 cm^{-1} are found to be shifted to higher energy, suggesting the increased bond order in C-N bond, which proves the involvement of the thioamidic group in coordination. The sulphur coordination is further supported by a shift of the strong band at 741.4 cm^{-1} and 713.7 cm^{-1}.
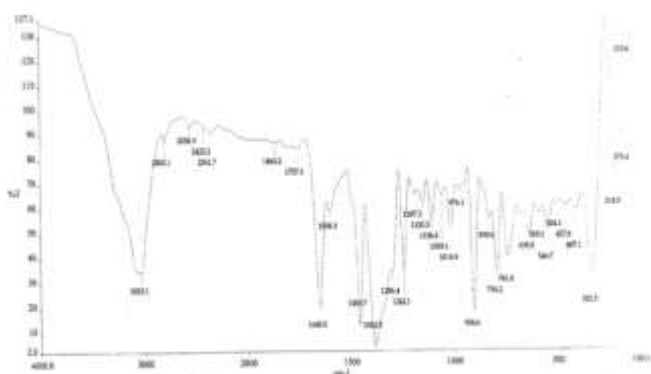

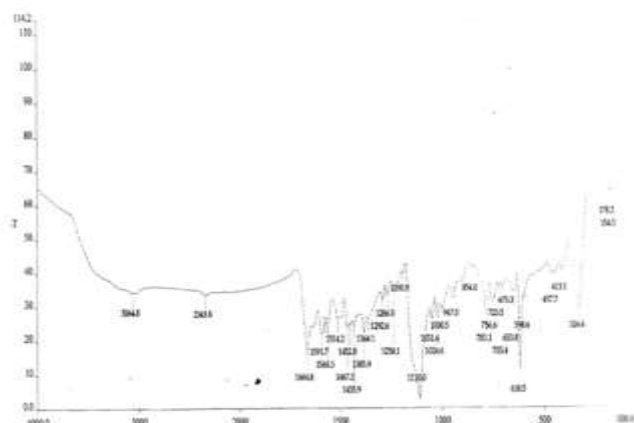**Fig. 1 - IR Spectrum of Nickel (II) complex of TPA**

Fig. 2 - IR spectrum of Nickel (II) complex of 2-N-benzyl TPA

In all the two complexes, water molecules are present either as water of crystallization alone or both as lattice water and water of crystallization which can be further evidenced by only the thermogravimetric studies. The region 218 cm^{-1} attributable to metal-sulphur stretching modes[10-12].

The infrared spectra of the complexes were recorded in the 4000- 200cm^{-1} regions and in some the 4000-600cm^{-1} and 625cm^{-1} region. The observed positions of the various bands in the case of the copper (II) complexes are given in Table 4 some of the typical spectra are reproduced in the Fig. 3 and 4.

The infrared spectra of all the copper (II) complexes show a broad peak in the 3000-3400cm^{-1} region indicating the presence of highly hydrogen bonded -NH$_2$ group or water molecules being present either as water of crystallization or lattice water. The existence of water of crystallization is also revealed by the presence of a sharp and split band around 1540-1570 cm^{-1}[13].

The bands observed for pyridine ring vibrations do not undergo perceptible change suggesting the non-involvment of pyridine nitrogen in the coordination.

The composite mode observed at 1540cm^{-1} and 1570cm^{-1} in the case of I and II respectively undergo a shift towards higher wave numbers clearly indicating sulphur coordination. It is supported by the fact that the composite mode at 1110cm^{-1} and 1265 cm^{-1} in the ligand molecules undergo a downward shift in the complexes towards lower wave numbers as evident from the

Tables. According to G.J. Sutton [14] which is further supported by weakening, complete disappearance or a negative shift of the band at 680cm^{-1}
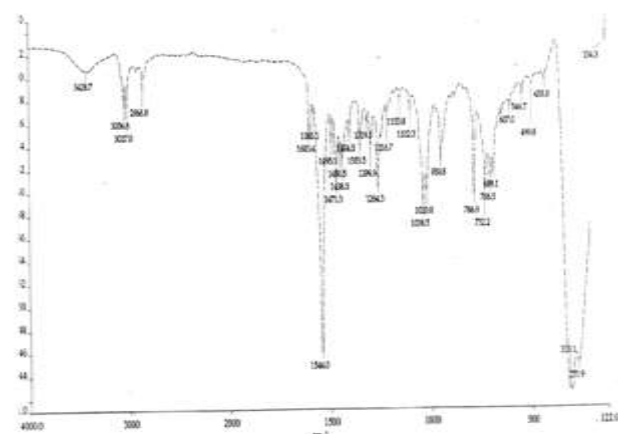

Fig. 3 - IR spectrum of Copper (II) complex of TPA

Fig. 4 - IR spectrum of Copper (II) complex of 2-N-benzyl TPA

Bands of medium intensity in the region 200-250cm^{-1} attributable to metal-sulphur stretching modes[15-17] for thiomide complexes are well characterised oserved in the 210cm^{-1}.

Conductivity Measurement

Conductance measurements were made in DMF solvent to determine the charge-type in the two nickel (II) complexes and the data are given in Table 5. The result are in agreement with the formula assigned form the analytical data. All the complexes happen to be bi-univalent type as is evident from the reported values of Geary [18].
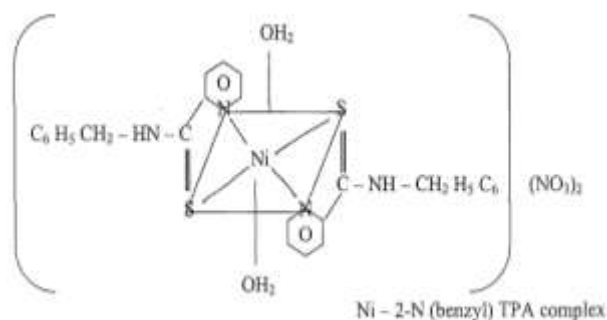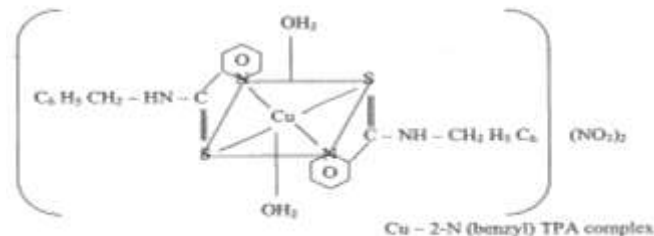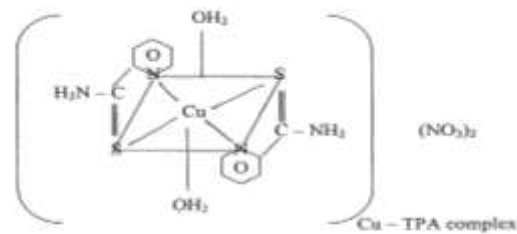
The conductance measurements were made in DMF solvent to determine the change type in the various complexes and the λ_M values are given the Tables 6 for the copper (II) complexes.

Results and Findings

1. The Ni (II) complexes formed are supposed to be octahedral in nature with two water molecules along the z-axis or distorted due to John Teller distortion reducing to square planar geometry.

2. Both the complexes are soluble in DMF indicative their ionic nature and excluding the possibility of polymeric complexes.

3. The ligands act as a bidentate neutral molecules and hence the net charge on the complexes is countered by the anion viz. nitrate.

4. The conductivity data indicate the bi-univalent behaviour of the complexes.

Based on the above findings, the nickel (II) complexes with both TPA and 2-N-benzyl TPA may be assigned the structure.

However the exact structure can be assigned only by confirming using x-ray and other studies.

Ni – TPA complex

Ni – 2-N (benzyl) TPA complex

1. The Cu (II) complexes formed are supposed to be octahedral in nature with two water molecules along the z-axis or distorted due to John Teller distortion reducing to square planar geometry.
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Cu – TPA complex

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Table - 1
Elemental analysis of Nickel (II) complexes

	Complex	Elements	Found	Calculated
1.	Nickel (II) Nitrate -TPA	Ni	11.6%	11.74%
		S	12.61%	12.95%
		N	17.2%	17.00%
2.	Nickel (II) Nitrate-2 -N-benzyl TPA	Ni	8.41%	8.6%
		S	9.2%	9.49%
		N	12.15%	12.46%

Table - 2
Elemental Analysis of Copper (II) Complexes

	Complex	Elements	Found	Calculated
1.	Copper (II) Nitrate-TPA	N	16.77%	17.00%
		S	12.5%	12.95%
		Cu	12.21%	12.75%
2.	Copper (II) Nitrate-2 -N-benzyl TPA	N	12.3%	12.46%
		S	9.32%	9.49%
		Cu	9.08%	9.34%

Table - 3
Characteristic IR frequencies (cm^{-1}) of the Nickel (II) complexes

Complex	ν_{N-H}	Composite band I^a	Composite band II^b	$\nu_{C=S}$	Pyridine ring modes		
					1	2	3
Ni-TPA	3032(Sh)	1598.3(m)	1242 (m)	741(m)	1649(s)	1014(m)	639(m)
Ni-2 -N-benzyl TPA	3248(br)	1542(m)	1284(m)	713(m)	1545(m)	1001(m)	502(m)

a : δ (NH) + ν (CN) + δ (CH)
b : ν (CN) + δ (NH) + δ (CH) + ν (CS)
Abbreviations
s : strong, m : medium, br : broad, sh : shoulder

Table - 4
Characteristic IR frequencies (cm^{-1}) of the Copper (II) complexes

Complex	ν_{N-H}	Composite bank I^a	Composite band II^b	$\nu_{C=S}$	Pyridine ring modes		
					1	2	3
Cu-TPA	3064 (sh)	1565 (m)	1110 (s)	749 m)	1592 (m)	1000 (w)	617 (s)
Cu-2 -N-benzyl TPA	3056 (m)	1544 (s)	1264 (m)	706 (m)	1585 (w)	1020 (w)	499 (w)

a : δ (NH) + ν (CN) + δ (CH)
b : ν (CN) + δ (NH) + δ (CH) + ν (CS)
Abbreviations
s : strong, m: medium, br : broad, sh : shoulder, w : weak

Table - 5
Conductivity data for Nickel (II) complexes

Complex	Solvent	λ_M mho cm^2 mol^{-1}	Type of electrolyte
Ni-TPA	DMF	136.7	Bi-univalent
Ni-2 -N-benzyl TPA	DMF	132.1	Bi-univalent

Table -6
Conductivity data for Copper (II) complexes

Complex	Solvent	λ_M mho cm^2 mol^{-1}	Type of electrolyte
Cu-TPA	DMF	143.1	Bi-univalent
Cu-2 -N-benzyl TPA	DMF	148.7	Bi-univalent