Synthesis, Spectral and Antimicrobial Screening of mixed ligand complexes of Co(II), Ni(II), Cu(II), Ru(II) and Zn(II) with Anthranilic acid and Tribenzylphosphine

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Abstract

Synthesis, Spectral Characterization and Antimicrobial screening of some mixed ligand complexes of Co(II), Ni(II), Cu(II), Ru(II) and Zn(II) with tribenzyl phosphine and anthranilic acid are investigated. The octahedral structure of bis-chelates are deduced using elemental analyses, conductivity measurements, IR, UV-vis and ^{1}H NMR studies. Anthranilic acid acts as mononegative bidentate chelating anion with these bivalent metal ions. The antimicrobial activities of ligand and complexes against three types of pathogenic bacteria, Staphylococcus, Klebsiella ssp and Bacillas are examined.

Key words : bivalent metal ions, Bis-chelates, antibacterial activities.

Introduction

The literature survey revealed that anthranilic acid has versatile coordinating ability and bio-activities.[1-2] There are many report on the metal anthranilate complexes.[3-5] The present study aims at synthesis, characterization and antimicrobial activity of some mixed ligand complexes of bivalent metal ions in continuation our investigations with this ligand.[6-8] The structure all new chelates are deduced on the basis of elemental analysis, magnetic moment, conductometric electronic, IR and ^{1}H NMR spectral data.

Experimental

All chemical used were of AR grade or CP grade. Solvents were dried before use. Tribenzylphosphine (PBz$_3$) was prepared using a modification of the reported method[9] as ivory coloured crystals. The precursor complex [RuCl$_2$(PBz$_3$)$_2$] was prepared following the reported method of Stephensen *et al.*[10] All new complexes were prepared using our previous method reported in literature[6] and their

analytical and physical data is given in table 1.

Anthranilic acid is commercial product obtained from E. Merck. The elemental analysis, IR. Electronic and ^1H NMR spectral data were performed by conventional method as we have reported earlier.[6]

Results and Discussion

The precursor complex [RuCl$_2$(PBz$_3$)$_4$] display ligand substitution reaction in ethanolic solution of benzene (1:1) and yielded [Ru(PBz$_3$)$_2$A$_2$] as :

$$RuCl_2(Bz_3)_4 + 2AH \xrightarrow[\text{reflux}]{C_6H_6/EtOH} [(Ru(Bz_3)_2A_2] + 2HCl + 2Bz_3$$
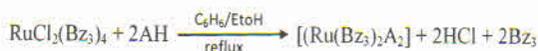
Metal salts as chloride react with sodium salt of anthranillic leading to the formation of other bivalent metal complexes :

$$2AH + 2KOH \longrightarrow 2K^+A^- + 2H_2O$$

$$MCl_2 + 2K^+A^- + 2PBz_3 \xrightarrow[\text{reflux}]{EtOH}$$

$$[MA_2(PBz_3)_2] + 2KCl$$
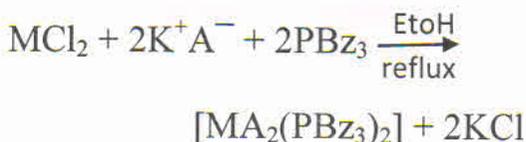
(M = Co(II), Ni(II), Cu(II) and Zn(II); AH = NH$_2$C$_6$H$_4$COOH)

All products were soluble in DMF and DMSO while insoluble in water. The observed molar conductance value in DMF (10^{-3}M) solution lies in the range $20.16 = 20.38 \wedge^{-1} cm^{-1}$ mol^{-1} indicating their non-electrolytic nature and agreement with literature value.[11]

Magnetic Moment and Electronic Spectra:

The ruthenium (II) complex is diamagnetic indicating spin pairing in Ru^{++} (d^6) in octahedral structure with ground state $^1A_{1g}$. The observed transitions $^1A_{1g} \to {}^1T_{1g}$ (19240 cm^{-1}) and $^1A_{1g} \to {}^1T_{2g}$ (14970 cm^{-1}) are similar to those other octahedral complexes.[12] The other high intensity bands at 25900 cm^{-1} (T$_{2g} \to \pi^*$) and at 39060 cm^{-1} ($\pi \to \pi^*$) are consistent with the pattern of electronic spectra of octahedral geometry around ruthenium ion.[13-14] The Cu(II) complex exhibits magnetic moments of 1.68 BM and one broad band with maxima at 14550 cm^{-1} ($^2E_g \to {}^2T_{2g}$) support a distorted octahedral configuration of complex.[15] The cobalt (II) complex exhibits magnetic moment of 4.73 BM indicating spin free octahedral structure.[16] The d-d transition bands observed at 8775 cm^{-1} (4T$_{1g}$ (F) $\to {}^4T_{2g}$ (F), v_1), 18185 cm^{-1} ($^4T_{1g}$ (F) $\to {}^4A_{2g}$ (F), v_2) and at 21885 cm^{-1} ($^4T_{1g}$ (F) $\to {}^4T_{1g}$ (F), v_3) are also supports octahedral considering previous literature.[16] The ligand field parameters Dq=940 cm^{-1}, B = 917 cm^{-1} and v_2/v_1=2.07 are in agreement with octahedral structure.[16] The Ni(II) complex shows magnetic moment of 3.15 BM and electronic spectrum exhibits four bands at 3570 cm^{-1} (CT Band), 9400 cm^{-1} ($^3A_{2g} \to {}^3T_{2g}$, v_1), 16510 cm^{-1} ($^3A_{2g} \to {}^3T_{1g}$ (F), v_2) and 25100 cm^{-1} ($^3A_{2g} \to {}^3T_{1g}$ (F), v_3) in a distorted octahedral field.[17] The ligand field parameters, Dq = 940 cm^{-1}, B = 806 cm^{-1} and v_2/v_1 = 1.75 also confirm the octahedral geometry for the complex.[18]

IR Spectra:

Anthranilic acid acts as mononegative

bidentate and forms M-O and M-N bonds in all complexes. The ν_{asym} (NH$_2$) and ν_{sym} (NH$_2$) in free anthranilic acid are observed at 3400 cm^{-1} and 3300 cm^{-1} red shift to lower frequency 35-40 cm^{-1} and 40-50 cm^{-1} respectively on complexation indicating formation of Metal-N bond. This is also corroborated by the presence of new bands in the range 520-535 cm^{-1} due to Metal-N stretching mode. The bands at 1700 cm^{-1} and 1560 cm^{-1} in free anthranilic acid assigned to ν_{asym} (COO) and ν (COO) suffered a major change to lower frequency and observed at 1620-1630 cm^{-1} and 1405-1410 cm^{-1} respectively in complexes suggest the presence of monodentate carboxylate group.[19-20] The formation of Metal-O bond is further supported by new non-ligand bands around 430-510 cm^{-1} due to Metal-O stretching mode. New bands in far-IR spectra of complexes around 420-425 cm^{-1} assigned due to νMetal-P bond.

¹H NMR Spectra:

The free anthranilic acid exhibits signals between δ7.72-6.52 (multiplet) PPM, δ8.4 PPM and at 3.6 PPM due to phenyl protons, amino protons and protons of –OH group respectively. The free tribenzyl phosphine exhibits signals at δ2.78 PPM and at δ7.15-6.32 PPM due to methylene protons and aromatic protons.

The amino protons are low field shifted on complexation and the integrated intensities of the signals agree with assigned structure of complexes. The phenyl protons signals are slightly low field shifted and –OH proton signals are not present in complexes

indicating deprotonation. Thus, on the basis of above observations the octahedral (I) is tentatively assigned for all six-coordinated complexes.
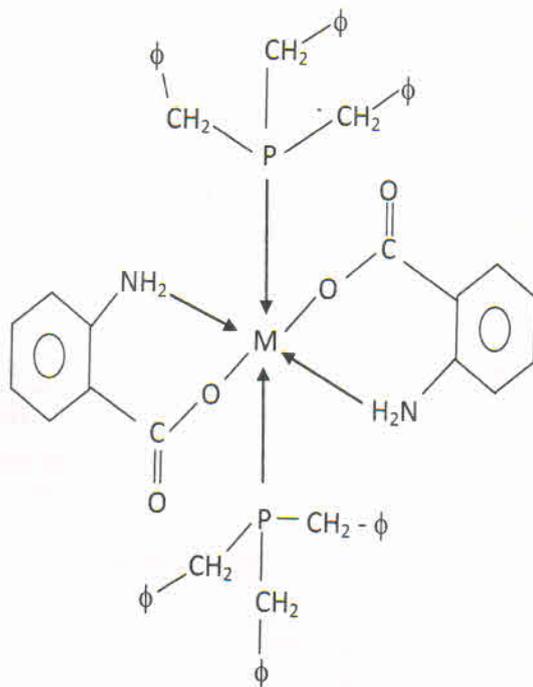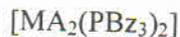
Octahedral structure of
[MA$_2$(PBz$_3$)$_2$]
(M = Ru(II), Co(II), Ni(II), Zn(II) & Cu(II);
AH = anthranilic acid)
(Str. I)

Antibacterial Activities:

Antimicrobial activities of ligands and complexes was carried out using disc diffusion methiod.[21] The test solution were prepared in DMSO and soaked in filter paper of 5 mm diameter and 1 mm thickness. These discs were placed on the already seeded plates and incubated at 37⁰C for 24 hours.[22] The zone of

Table 1. Analytical and Physical Data of Complexes

S. No.	Complex	Analysis (%) : Found/(Calcd)				μeff (BM)	Molar conductance Ohm^{-1}cm^{2}mol^{-1}
		Metal	C	H	N		
1.	[RuA$_2$(PBz$_3$)$_2$]	10.39 (10.29)	68.62 (68.50)	5.51 (5.50)	2.96 (2.85)	Diamag.	28.16
2.	[CuA$_2$(PBz$_3$)$_2$]	6.75 (6.73)	71.32 (71.22)	5.72 (5.73)	3.01 (2.96)	1.68	20.28
3.	[CoA$_2$(PBz$_3$)$_2$]	6.33 (6.23)	71.67 (71.57)	5.77 (5.75)	3.01 (2.98)	4.73	22.20
4.	[NiA$_2$(PBz$_3$)$_2$]	6.21 (6.25)	71.60 (71.58)	5.77 (5.75)	3.20 (2.98)	3.15	22.46
5.	[ZnA$_2$(PBz$_3$)$_2$]	6.92 (6.91)	71.18 (71.08)	5.77 (5.71)	3.22 (2.96)	Diamag.	20.12

Table 2. Major IR and ^{1}H NMR spectral data of ligands and complexes

Comp- ounds	IR (cm^{-1})			^{1}H NMR (δ PPM)				
	v_{asym} NH$_2$/ (v_{sym} NH$_2$)	v_{asym} COO/ (v_{sym} COO)	vM-N/ (vM-O)	Amino protons	Phenyl protons	OH proton	CH$_2$ proton	Aromatic proton
AH	3400 s (3300 s)	1710 s (1560 s)	- (-)	8.40	7.72 – 6.52	3.6	-	-
PBz$_3$	- (-)	- (-)	- (-)	- (-)	- (-)	-	2.78	7.15 – 7.32
Ru (II) (Sl. No. 1)	3360 s (3270 s)	1680 s (1470 m)	565 m (505 m)	8.32	7.72 – 6.52	-	2.88	7.16 – 7.40
Cu (II) (Sl. No. 2)	3360 ms (3265 ms)	1690 s (1475 m)	550 m (510 w)	8.31	7.68 – 6.80	-	2.87	7.15 – 7.41
Co (II) (Sl. No. 3)	3320 s (3225 m)	1690 s (1485 m)	520 m (505 w)	8.32	7.70 – 6.80	-	2.86	7.16 – 7.27
Ni (II) (Sl. No. 4)	3330 s (3250 m)	1690 s (1475 m)	525 w (510 w)	8.32	7.70 – 6.80	-	2.86	7.16 – 7.27
Zn (II) (Sl. No. 5)	3345 s (3235 m)	1685 m (1475 m)	532 w (505 w)	8.30	7.72 – 6.82	-	2.88	7.12 – 7.41

Table 3. Inhibition circle diameter in mm for the bacteria after 24 hours
incubation paid at 37^0C for complexes

Compounds	Bacillus	Klebsiella ssp	Staphylococcus
Contro DMSO	10.8	9.9	13.4
AH	17.9	14.1	20.6
PBz₃	13.1	12.9	16.2
Ru (II)(Sl. No. 1)	18.1	14.2	21.2
Cu (II)(Sl. No. 2)	20.3	17.3	20.2
Co (II)(Sl. No. 3)	18.7	15.9	28.7
Ni (II)(Sl. No. 4)	20.5	18.2	20.3
Zn (II)(Sl. No. 5)	20.2	15.4	21.3

inhibition of bacterial growth is given in table 3. The antibacterial activity results revealed that complexes have more pronounced activities than ligands due to chelation.[23-25]

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