Int. J. Chem. Sci.: 11(3), 2013, 1464-1470
ISSN 0972-768X
www.sadgurupublications.com

METAL DERIVATIVES OF ORGANO-PHOSPHOROUS COMPOUNDS LIGATED BY ANTHRANILIC ACID

R. N. PANDEY* and RAKESH RANJAN

P.G. Centre of Chemistry (M.U.), College of Commerce, PATNA – 800020 (Bihar) INDIA

ABSTRACT

Mixed ligand complexes of Ru(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) of composition $[MA_2(P\phi_3)_2]$ with anthranilic acid (AH) and triphenyl phosphine ($P\phi_3$) have been prepared and characterized by elemental analyses, conductivity measurements, IR, UV-vis and ^1H NMR studies. The anthranilic acid acts as bindentate anion and triphenyl phosphine as neutral monodentate. The octahedral configuration of all six-coordinated complexes are tentatively assigned.

Key words: Bivalent Metal ions, Anthranilic acid, Triphenyl phosphine, Metal-ligand vibrations.

INTRODUCTION

The literature survey revealed that anthranilic acid has excellent coordinating ability and bio-activities[1,2]. The thermodynamic and electrical propeties of aminophenol and anthranilic acid complexes with some transition metals are reported by Wahed et al.[3] Borowski and Cole-Hamilton[4] have examined structures and properties of Anthranilato and N-phenyl anthranilatorhodium(1) complexes containing triphenyl phopsphine. There are many report on the metal anthranilate complexes[5-7]. The present study aims at synthesis and spectral characterization of metal derivatives of organo-phosphorous compounds ligated by anthranilic acid.

EXPERIMENTAL

All chemical used were of AR grade or CP grade. The anthranilic acid and triphenyl phosphine were obtained from E. Merck. Solvents were dried before use. The precursor complex $[RuCl_2(P\phi_3)_4]$ was prepared by the method reported in literature[8].

*Author for correspondence; E-mail: rameshwarnath.pandey@yahoo.com, dr_rranjan@yahoo.com; Mob.: 09931886399, 09431201187

Preparation of complexes

S. No. 1 $[Ru(P\phi_3)_2A_2]$

A benzene solution of $[RuCl_2(P\phi_3)_4]$ (1 mmol) was added to ethanolic solution of anthranilic acid (2 m mol) and triphenyl phosphine (2 mmol). The resulting mixture was refluxed on a water bath for about 2 hr. and filtered hot. The pH of the mixture was made 7.5 using 50% aquous solution of NaOH and ethanol. The solution was concentrated to 15 mL and addition of 15 mL petrolium ether, the separated solid was filtered and dried over anhydrous $CaCl_2$ in a desiccator (yield = 67%).

S. No. 2 to 5 $[M(P\phi_3)_2A_2]$

(M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, A = Anthranilate ion)

An aquous solution of metal chloride (1 mmol) was added gradually with stirring to ethanolic potassium anthranilate (2 mmol.) and triphenyl phosphine (2 mmol). The mixture was refluxed with constant stirring for an hour. The mixture was concentrated (20 mL) and cooled and separated solid was filtered and recrystillized from ethanol and dried (yield = 75%).

The C, H and N analysis were performed by conventional methods and results are given Table 1.

Table 1: Analytical and physical data of complexes

S. No.	Complex/ (colour)	Analysis (%) : Found / (Calcd)				$M_{eff.}$ (BM)	Molar Cond. $Ohm^{-1}\ cm^2\ mol^{-1}$
		C	H	N	Metal		
1	$[RuA_2(P\phi_{3)2}]$ (Brown)	68.72 (68.89)	4.60 (4.68)	3.33 (3.12)	11.31 (11.25)	dia. Mag.	22.32
2	$[CuA_2(P\phi_{3)2}]$ (Blue)	69.92 (69.80)	4.89 (4.88)	3.35 (3.25)	7.45 (7.39)	1.67	32.50
3	$[CoA_2(P\phi_{3)2}]$ (Green)	70.22 (70.18)	5.01 (4.91)	3.43 (3.27)	7.01 (6.89)	4.72	21.72
4	$[NiA_2(P\phi_{3)2}]$ (Yellowish green)	70.31 (70.20)	5.01 (4.91)	3.15 (3.27)	6.92 (6.86)	3.15	18.68
5	$[ZnA_2(P\phi_{3)2}]$ (Yellow)	69.82 (69.65)	4.88 (4.87)	3.20 (3.25)	7.62 (7.59)	dia. Mag.	28.10
6	$[CdA_2(P\phi_{3)2}]$ (Yellow)	66.27 (66.07)	4.72 (4.62)	3.21 (3.08)	12.36 (12.34)	dia. Mag.	21.11

IR Spectra of ligands and complexes were recorded with the help of Perkin Elmer Model 621 in the range of 4000-200 cm^{-1} using KBr pellets technique. The magnetic measurements were made on gouy balance using $Hg[CO(SCN)_4]$ as calibrant. ^1H NMR Spectra of ligands and complexes were recorded on a high resolution varian HR-100 (cross coil type) NMR Spectrometer in $CDCl_3$ solution. Electronic Spectra (10^{-3} M DMF) were recorded using Hilger watt Uvispeck spectrophotometer.

RESULTS AND DISCUSSION

$RuCl_2(P\phi_3)_4$ undergoes ligand substitution reaction :

$$RuCl_2(P\phi_3)_4 + 2\ AH \xrightarrow[EtOH]{C_6H_6} [Ru(P\phi_3)_2A_2] + 2\ HCl + 2\ P\phi_3$$

Metal salts as chloride react with ligands leading to the formation of other complexes :

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

$$MCl_2 + 2\ A^-\ K{+}\ 2\ P\phi_3 \xrightarrow{EtOH} [MA_2(P\phi_3)_2] + 2\ KCl$$

(M = Co(II), Ni(II), Zn(II), Cd(II), AH = $NH_2C_6H_4COOH$)

The products have been purified by crystallization and have been fully characterized by means of elemental analysis, IR, NMR Spectroscopies and other physico-chemical measurements. All products were soluble in DMF and DMSO while insoluble in water. The observed molar conductance values in DMF in 10^{-3} M solution lies in the 20.80-32.50 Ω^{-1} cm^2 mol^{-1} range indicated their non-electrolytic nature[9].

Magnetic moment and electronic spectra

The magnetic moments obtained at room temperature for complexes are listed in Table 1.

The cobalt (II) complex shows magnetic moment of 4.72 BM indicating spin free octahedral structure[10]. The ligand field bands are observed at 8770 cm^{-1} ($^4T_1g(F) \rightarrow {}^4T_2g(F)$, υ_1), 18185 cm^{-1} ($^4T_1g(F) \rightarrow {}^4T_2gF$, υ_2) and at 21880 cm^{-1} (^4T_1g (F) $\rightarrow {}^4T_1g(P)$, υ_3). The ligand field Parameters like Dq = 941 cm^{-1}, B = 917.00 cm^{-1}, B_{35} = 0.94 and V_2/V_1 = 2.07 also suggest octahedral stereochemistry for the complex[10]. The Nickel (II) complex shows magnetic moment of 3.15 BM and electronic spectrum exhibit four ligand field bands at 35715 cm^{-1} (CT band), 9400 cm^{-1} ($^3A_2g \rightarrow {}^3T_2g$, V_1), 16500 cm^{-1} ($^3A_2g \rightarrow {}^3T_1g(F)$, V_2) and

25100 cm^{-1} ($^3A_2g \rightarrow {}^3T_1g(P)$, V_3) in a distorted octahedral symmetry field[11]. The ligand field parameters like Dq = 940 cm^{-1}, B = 806 cm^{-1}, B_{35} = 0.78 and V_2/V_1 = 1.75 also confirm the octahedral geometry for the complex[12]. The Cu(II) complex exhibits magnetic moments of 1.67 BM and one broad band with maxima at 14540 cm^{-1} ($^2Eg \rightarrow {}^2T_2g$) support a distorted octahedral configuration of complex[13]. The ruthenium(II) complex is diamagnetic indicating spin pairing in Ru^{2+} (d^6) having normal octahedral structure with ground state $1A_1g$ and two spin allowed transitions $^1A_1g \rightarrow {}^1T_1g$ and $1A_1g \rightarrow {}^1T_2g$ are expected. These transitions are observed at 19230 cm^{-1} ($^1A_1g \rightarrow {}^1T_1g$) and 149970 cm^{-1} ($^1A_1g \rightarrow {}^1T_2g$) are agreement with previous literature[14-16]. The other band at 25974 cm^{-1} assigned to $T_2g \rightarrow \pi^*$ transition.

IR Spectra

A comparison of IR Spectra of anthranilic acid, triphenyl phosphine and complexes indicate the formation of Metal-O and Metal-N and Metal-P bonds. Anthranilic acid acts as mononegative bidentate. The υ_{asyam} (NH_2) and υ_{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 40-45 cm^{-1}, respectively indicating formation of Metal-N bond. This is also corroborated by the presence of new bands in the range of 520-535 cm^{-1} due to metal- N stretching mode. The bands at 1700 cm^{-1} and 1560 cm^{-1} in the spectrum of anthranilic acid assigned to υ_{asym}(COO) and υ_{sym}(COO) suffered a major change to lower frequency and observed at 1620-1630 cm^{-1} and 1405-1415 cm^{-1} respectively in complexes suggest the presence of monodetate carboxylate group[17,18]. The formation of metal oxygen bond is further Supported by non-ligand, new bands around 430-510 cm^{-1} due to metal-O stretching mode.

Triphenyl phosphine exhibits large number of bands in far-IR Spectrum[19,20]. The new band around 416-420 cm^{-1} is assigned to υ M-P mode of coordinated triphenyl phosphine.

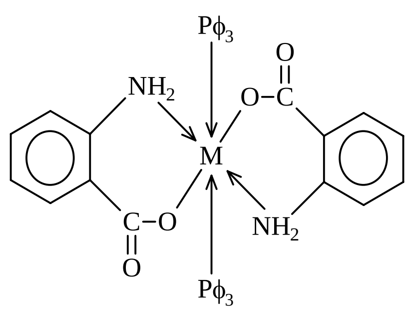
^{1}H NMR Spectra

The free anthranilic acid exhibits signals at δ 7.72-6.52 (multiplet) PPM, δ 8.4 PPM and δ 3.6 PPM due to phenyl protons, amino protons and protons of –OH group, respectively. The amino protons signals are low field shifted on compexation and the integrated intensties of the signals agree with the assigned octahedral structure (I) of complexes. The phenyl protons signals are slightly low field shifted and the –OH proton signals are not present in complexes indicating deprotonation. The signals found at δ 8.70-8.10 PPM as broad multiplet in complexes are due to aromatic protons of coordinated $P\phi_3$ molecules[21] and the integrated intensitives agree well with the formulation of complexes.

Table 2: Major IR and ^{1}H NMR spectral data of ligand and complexes

Compds.	IR (cm^{-1})				^{1}H NMR (δPPM)			Aromatic Pφ$_3$ protons
	υ_{asym} NH$_2$/υ_{sym} (NH$_2$)	υ_{asym}(COO)/ υ_{sym}(COO)	υ M-N/ (υM-O)	υ M-P	Amino proton	Phenyl proton	Protons of –OH gr.	
Anthranilic Acid (AH)	3400 S (3300 S)	1710 S (1560 ms)	(-)	(-)	8.40	7.72-6.52 (multiplet)	3.6	(-)
Ru(II) (S. No. 1)	3360 S 3270 S	1685 S (1475 m)	560 m (510 w)	420 w	8.30	7.72-6.52	-	8.70
Cu(II) (S. No. 2)	3355 S 3265 M	1691 S (1477 m)	550 m (510 w)	425 w	8.32	7.70-6.8	-	8.10
Co(II) (S. No. 3)	3314 S 3220 S	1695 S (1485 m)	520 w 505 w	415 w	8.31	7.72-6.80	-	8.68
Ni(II) (S. No. 4)	3350 S 3250 S	1690 S (1475 S)	525 w (510 w)	410 w	8.32	7.78-6.85	-	8.15
Zn(II) (S. No. 5)	3325 S 3126 S	1680 S (1472 S)	532 w (510 w)	415 w	8.31	7.72-6.82	-	8.55
Cd(II) (S. No. 6)	3370 S 3265 S	1685 S (1470 m)	515 w (450 w)	420 w	8.34	7.76-7.10	-	8.25

Thus, on the basis of above observations the octahedral structure (I) is tentatively assigned for all six- coordinated complexes.



Octahedral Structure of [MA$_2$(Pφ$_3$)$_2$]

(M = Ru(II), Co(II), Ni(II), Zn(II) & Cd(II), AH = Anthranilic acid)

(Structure 1)

REFERENCES

1. N. Raman, J. Joseph, S. Muthy Kumar, S. Sugatha and K. Sahayaraj, J. Biopesticides, **1(2)**, 206 (2008).
2. Taghreed, H. Al-Noor, Khalid F. Ali, Amer J. Jarad and Aliea S. Kindeel, Chem and Materials Res., **3(3)**, 126 (2013).
3. Abd EI wahed, S. M. Metwally, M. M. EI Gamel and S. M. Abd. EL Haleem, Bull. Korean Chem. Soc., **22(7)**, 663 (2001).
4. A. F. Borowski and D. J. Cole- Hamilton, Polyhedron, **12**, 1757 (1993).
5. Taghreed H. Al-Noor, Ibtisam Dawood and Ibtihaj K. Malih, Int. J. Sci. Technol., **7(3)**, 32 (2012).
6. N. Raman, J. Joseph and K. Rajasekaram, Polish J. Chem., **81**, 149 (2007).
7. Rita Roy, K. Subrata Panchanan and Prag S. Roy, Transition Met. Chem., **12**, 137 (1987).
8. T. A. Stephensen and G. Wilkinson, J. Inorg. Nucl. Chem., **28**, 945 (1966).
9. W. J. Geary, Coord. Chem. Rev., **7(1)**, 81 (1971).
10. A. B. P. Lever, Coord. Chem. Rev., **3**, 119 (1963).
11. Liwang Jiwen Cai, Zon-Wang MaO, Xiao-long Feng and Jim-Wang Hyang, Trans. Met. Chem., **29**, 418 (2004).
12. H. Bipin B. Mahapatra and A. K. Sarangi, J. Indian Chem. Soc., **86**, 559 (2009).
13. S. Yamada, Coord Chem. Rev., **1**, 415 (1966).
14. R. N. Pandey, K. Shahi and P. Pandey, J. Ultra Chem., **7(3)**, 321 (2011).
15. T. Singh and J. P. Singh, J. Indian Chem. Soc., **69**, 158 (1992).
16. R. N. Pandey and K. V. Gautam, J. Ultra Chem., **7(1)**, 9 (2011).
17. N. F. Curtis, J. Chem. Soc., **4**, 1579 (1968).
18. B. Mahapatra, P. K. Bhoi, S. K. Kar and S. R. Prasad, J. Indian Chem. Soc., **72**, 399 (1995).
19. K. Shobatake, C. Postmus, J. R. Ferraro and K. Nakamoto, Appl. Spectro Sc. **23**, 12 (1969).

20. D. H. Brown, A. Mohamad and D. W. A. Sharp, Spectrochim, Acta., **21**, 663 (1965).

21. M. Chandra, A. N. Sahay, D. S. Pandey, M. C. Purerta and P. Valerga, J. Organometallic Chem., **648**, 39 (2002).

Accepted : 21.07.2013