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Synthesis, Characterization and antibacterial activity of mixed ligands complexes of some metal ions with 2-aminophenol and tributylphosphine.

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ABSTRACT

Four metal complexes mixed ligand of 2-aminophenol (2-AP) and tributylphosphine (PBu_3) were produced in aqueous ethanol with (1:2:2) (M:2-AP:PBu_3). The prepared complexes were identified by using flame atomic absorption, FT.IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. In addition antibacterial activity of the two ligands and mixed ligand complexes oboist three species of bacteria were also examined. The ligands and their complexes show good bacterial activities. From the obtained data the octahedral geometry was suggested for all prepared complexes.

Keywords: Mixed ligand complexes, spectral studies, 2-aminophenol, tributylphosphine.

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INTRODUCTION

Bioactive donor of N,S and O atoms in organic ligand moieties were widely used in the development of metal based drugs, clinical analytical areas, industrial, , agricultural, medical and biological importance (1,2). 2-aminophenol is widely used in oxidative hair dye formulations (3,4). Mixed ligand complexes have been found to act as an active catalyst in reactions of industrial importance including oxidative hydrolysis hydro formation and hydrogenation, of olefins and carboxylation of methanol. These complexes have also shown catalytic activity in various oxidation reactions of environmental importance(5). While many metals, such as Cu, Zn and Fe are essential for human health and protect us against many diseases, they are also implicated as being involved in many degenerative diseases including atherosclerosis (heart disease and stroke). Metals are essential to all forms of life (6).

The present paper reports the synthesis and characterization of new Co(II),Ni(II),Cu(II)and Zn(II) complexes with mixed ligand of 2-aminophenol and tributylphosphine.

EXPERIMENTAL

Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV-160 A) Ultra Violet-Visible Spectrophotometer. I.R-spectra were taken on a (Shimadzu, FTIR-8400 S) Fourier Transform Infrared. Spectrophotometer (4000-400) cm^{-1} with samples prepared as KBr discs. Atomic Absorption was obtained by using a (Shimadzu A.A-160A) Atomic Absorption / Flame Emission Spectrophotometer. Conductivities were measured for 10^{-3}M of complexes in DMSO at 25°C by using (Philips PW- Digital Conduct meter). Magnetic properties were performed by using Auto Magnetic Susceptibility Balance Sherwood Scientific instrument at 25C°. In addition, melting points were obtained by using (Melting Point Apparatus).

Materials

The following chemicals were used as received from suppliers; cobaltous chloride hexahydrate 98.8%, nickel chloride hexahydrate 99.9%, copper chloride dihydrate 98%, zinc chloride 98.8% (Merck), 2-aminophenol and tributylphosphine (B.D.H).

Study of Biological Activity

Three choice species of bacteria were used in this study *Escherichia Coli (E.Coli)* as Gram Negative Bacteria, *Staphylococcus Aureus (Staph. Aurous)* as Gram Positive Bacteria and *Morganella Marganii* in Neutrient Agar medium, using (DMSO) as a solvent and as a control, the concentration of the compounds in this solvent was 10^{-3}M, using disc sensitivity test. This way involves the exposure of the zone of inhibition toward the diffusion of micro- organism on agar plate. The plates were incubated for 24hrs at 37C°.

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing 0.118g, 0.118g, 0.085g and 0.068g (1mmole) of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ respectively was added gradually with stirring to ethanolic NaOH solution (0.109g,2mmol) of 2-aminophenol (sodium phenolate). (0.5ml,2mmole) of tributylphosphine (PBu_3) was added to the mixture in each case by using stoichiometric amount (1:2:2) Metal:2-AP:PBu_3 molar ratio. The mixture was refluxed with constant stirring for an hour. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystallized from ethanol and dried at room temperature leading to the following reaction at scheme -1.

RESULTS AND DISCUSSION

The ligand (2-AP) was characterized by FT.IR and UV-Vis. The solid complexes were produced by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions and tributylphosphine in a (M:L:PBu_3) of (1:2:2). The metal contents of these complexes were in good agreements with the calculated

values (Table-1) includes the physical properties. The molar conductance of the complexes as (10^{-3} M) in DMSO containing non-electrolytic type[7], the data were tabulated in (Table- 1).

UV-Vis spectra and magnetic properties of $[Co(2\text{-}AP)_2(Pbu_3)_2]$complexes

The UV-Vis spectra of the ligands and their complexes are included in (Table-2). The UV-Vis spectrum of the ligand (2-AP) shows three peaks, the first and second at 239 and 273 nm which were assigned to (π–π*), the third peak at 429 nm due to (n–π*) electronic transitions(8). The electronic spectrum of tributylphosphine display absorption peak at 297 nm was described to (π – π*)(9). The spectrum of Co(II) complex shows five peaks, the first peak at 236 nm which was described to ligand field, and second peak at 431 nm was assigned to charge transfer. Other three peaks at 639,730 and 951 nm which were attributed to electronic transition type $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$, $^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ and $^4T_{1g(F)} \rightarrow {}^4T_{1g(F)}$ respectively, also the value of the magnetic moment at 4.63 B.M may be taken as additional evidence for octahedral geometry (10). The electronic spectrum of Ni(II) complex appeared five absorption peaks, the first and second peaks at 238 and 433 nm due to ligand field and charge transfer sequences. Other three peaks at 532,782 and 952 nm which were assigned to electronic transition type $^3A_{2g} \rightarrow {}^3T_{1g(P)}$ and $^3A_{2g} \rightarrow {}^3T_{1g(F)}$ continuity. The magnetic moment of this complex was found at 2.92 B.M which was very close to the octahedral environment (11). The electronic spectrum of Cu(II) complex appears three peaks, the first and second at 239 and 432 nm due to ligand field and charge transfer, the third peak at 952 nm which was described to electronic transition type $^2E_g \rightarrow {}^2T_{2g}$. The magnetic moment of this complex was found at 1.76 B.M which was very close to the octahedral environment (12). The electronic spectrum of Zn(II) complex do show the charge transfer, and the magnetic susceptibility appeared the complex has diamagnetic moments, because d-d transition are not possible hence electronic spectrum did not give any fruitful information, in fact this result is a good agreement with previous work of octahedral geometry (13,14).

Fourier transforms infrared spectra of the mixed ligand complexes

The relevant vibration bands of the free ligands and their complexes were recorded in KBr in the region 4000-400 cm^{-1}. The assignments of the characteristic bands (FT-IR) spectra for free ligand, 2-aminophenol, tributylphosphine and complexes are summarized in Table-3. The IR spectrum of the ligand (2-AP) display broad band at 3464 cm^{-1}, which was described to the stretching vibration of υ(OH) phenol, this band was disappear in the spectra of all produced complexes, which attributed coordination this band with metal ion(15). The bands at 3375 cm^{-1} and 3302 cm^{-1} were assigned to ν(NH_2) stretching frequency(16), on complexation a shifting with change in shape were observed from these bands, while increasing in intensity were noticed, indicated may be a result of coordination with metal ion. The bands in IR spectrum of the ligand at 16oo cm^{-1} and 1512 cm^{-1} due to stretching vibration of υ(C=C)(17). The new bands noticed at (540-428) cm^{-1} are tentatively assigned to ν(M-N),ν(M-O) and ν(M-P) (Metal-Ligands) stretching bands(18,19).

According to the results obtained and spectral analysis an octahedral geometry has been suggested for produced complexes.

Finally, the antibacterial activity of the ligand and their complexes have also been examined oboist choice selected species of bacteria, (Table-4)and figure (1) show the deactivation capacity oboist against the bacteria specimen of the produced compounds under study.

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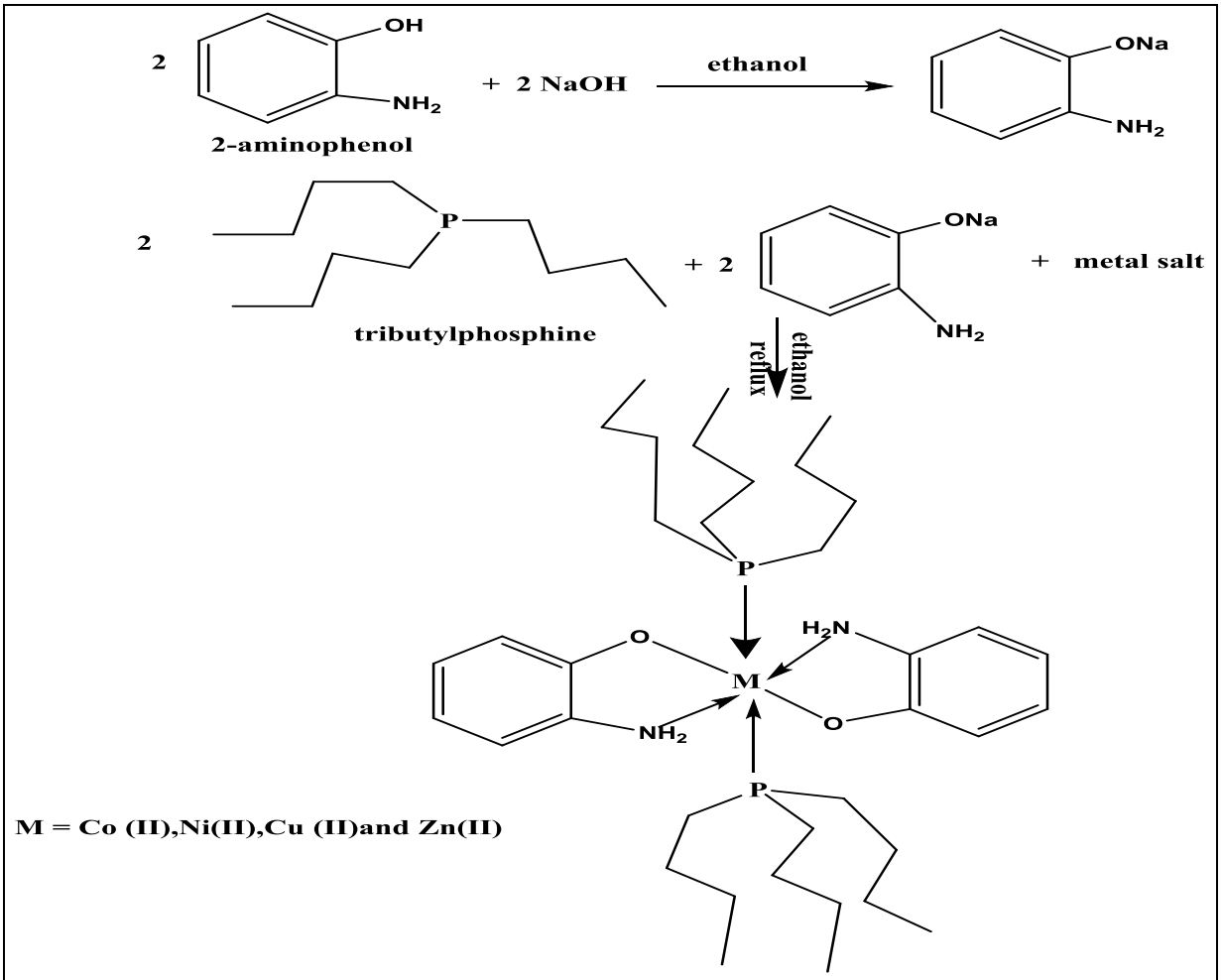

Scheme-1: The expected geometry of the metal(II) complexes $[M(2\text{-}AP)_2(PBu_3)_2]$.

Table (1): Physical properties of the ligand and it's complexes.

Compounds	Color	M.P °C	Yield%	M%	Λ_m ($S.cm^2.mol^{-1}$) in DMSO(10^{-3}M)	μ_{eff} (B.M)
Ligand(2-AP)	Yellow	183-185	-	-	-	-
$[Co(2\text{-}AP)_2(Pbu_3)_2]$	Deep brown	234-242	73	8.66 (7.88)	18.64	4.63
$[Ni(2\text{-}AP)_2(Pbu_3)_2]$	Brown	253-255	77	8.62 (7.79)	20.62	2.92
$[Cu(2\text{-}AP)_2(Pbu_3)_2]$	Brown	264-266	76	9.33 (8.93)	25.17	1.76
$[Zn(2\text{-}AP)_2(PBu_3)_2]$	Brown	227-279	75	9.46 (8.85)	17.38	Dia

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Table (2): UV-Vis spectral data for the ligands and their complexes.

Compounds	λ_{max} (nm)	ABS	Wave number (cm^{-1})	ϵ_{max} ($L.mol^{-1}.cm^{-1}$)	Remarks
Ligand(2-AP)	239 273 429	2.276 2.388 0.333	41841 36630 23310	2276 2388 333	$(\pi - \pi^*)$ $(n - \pi^*)$
PBu_3	297	0.609	33670	609	$(\pi - \pi^*)$
$[Co(2\text{-}AP)_2(Pbu_3)_2]$	236 431 693 730 951	1.245 0.829 0.103 0.088 0.011	42372 23301 14430 13698 10515	1245 829 103 88 11	L.F C.T $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ $^4T_{1g(F)} \rightarrow {}^4A_{2g(f)}$ $^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$
$[Ni(2\text{-}AP)_2(Pbu_3)_2]$	238 433 532 782 952	2.344 1.674 0.473 0.077 0.006	42016 23094 18796 12787 10504	2344 1674 477 77 6	L.F C.T $^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$ $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ $^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$
$[Cu(2\text{-}AP)_2(Pbu_3)_2]$	239 432 952	2.203 1.635 0.035	41841 23148 10504	2203 1635 35	L.F C.T $^2E_g \rightarrow {}^2T_{2g}$
$[Zn(2\text{-}AP)_2(PBu_3)_2]$	236 283 345 360	1.854 0.739 2.144 1.331	42372 35335 28985 27777	1854 739 2144 1331	C.T C.T C.T C.T

Table (3): The main frequencies of the ligands and it's complexes (cm^{-1}).

Compounds	υ(OH)	υ(NH_2)	υ(C=C)	υ(M-N)	υ(M-O)	υ(M-P)
Ligand(2-AP)	3464 br.	3375 s. 3302 s.	1600 s. 1512 s.	-	-	-
$[Co(2\text{-}AP)_2(Pbu_3)_2]$	-	3406 br.	1603 sho 1516 sho.	540 w.	509 w.	486 w.
$[Ni(2\text{-}AP)_2(Pbu_3)_2]$	-	3407 br.	1604 s. 1508 s.	509 w.	482 w.	451 w.
$[Cu(2\text{-}AP)_2(Pbu_3)_2]$	-	3406 br.	1600 s. 1504 sho.	501 w.	476 w.	428 w.
$[Zn(2\text{-}AP)_2(PBu_3)_2]$	-	3402 br.	1612 s. 1516 s.	532 w.	482 w.	439 w.

sho=shoulder, s = strong, w =weak, br = broad

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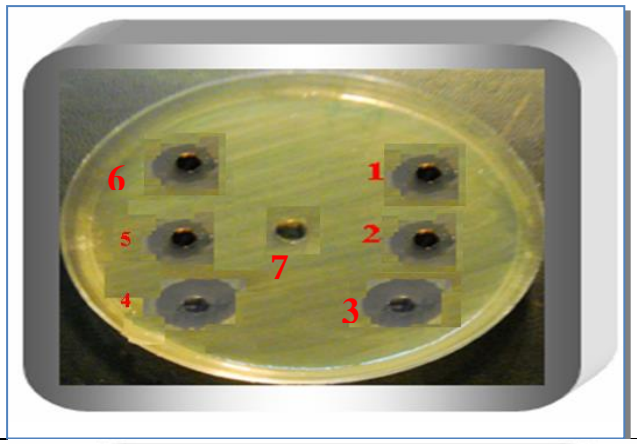
Table (4): Diameters (mm) of deactivation of bacteria for compounds

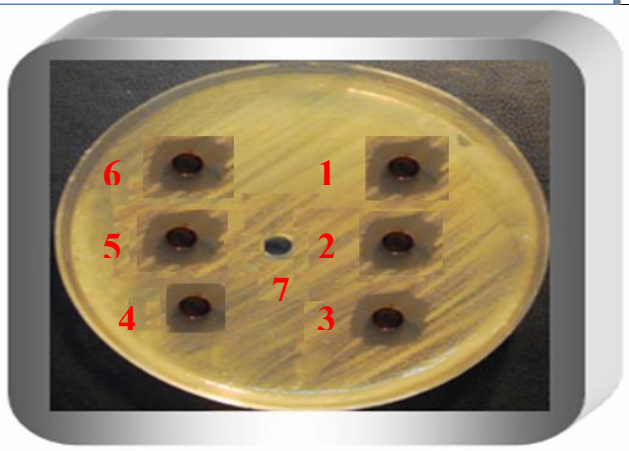
Compounds	*Morganella Marganii*	*Staphylococcus Aurous*	*Escherichia Coli*
control	6	4	5
Ligand(2-AP)	33	37	28
PBu_3	22	30	32
$[Co(2\text{-}AP)_2(Pbu_3)_2]$	38	28	32
$[Ni(2\text{-}AP)_2(Pbu_3)_2]$	36	27	22
$[Cu(2\text{-}AP)_2(Pbu_3)_2]$	25	32	24
$[Zn(2\text{-}AP)_2(PBu_3)_2]$	22	36	32

Moganella Mogarganii

i



(B):- ***Staphylococcus auros***



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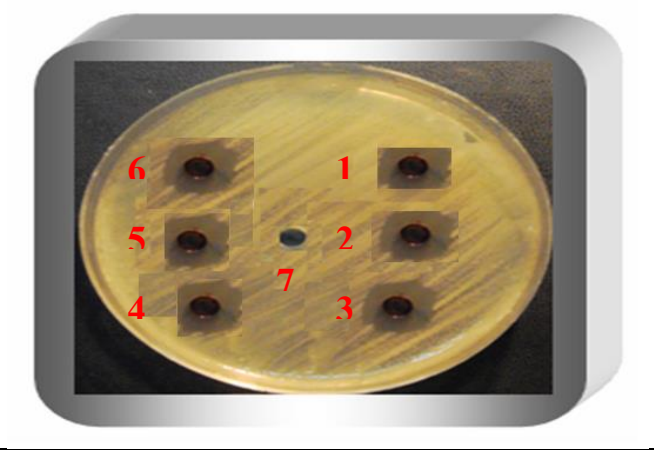
(C):- *Esherichia Coli*



1- (2-AP), 2- (Pbu_3), 3- [$Co(2\text{-}AP)_2(PBu_3)_2$], 4- [$Ni(2\text{-}AP)_2(PBu_3)_2$] 5-[$Cu(2\text{-}AP)_2(PBu_3)_2$] 6-[$Zn(2\text{-}AP)_2(PBu_3)_2$] ,
7 control(DMSO).

CONCLUSION

Mixed ligand complexes can be a synthetic challenge to tune the properties of the metal complexes .and have been shown to exhibit a broad range of The possible geometry of synthesized complexes is octahedral and it is six coordinated metal ligand complexes.

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