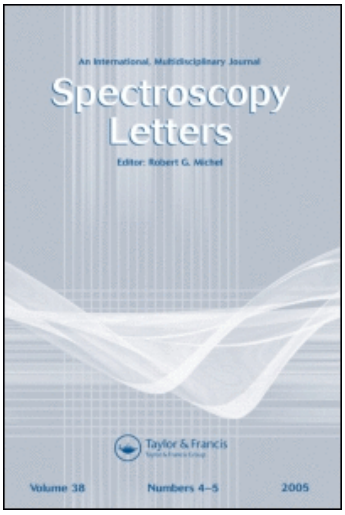

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Synthesis and Characterization of New Cationic Fe(III),Co(II) and Ni(II) Complexes Containing Isatin/Triphenylphosphine Mixed Ligands

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SYNTHESIS AND CHARACTERIZATION OF NEW CATIONIC Fe(III),Co(II) and Ni(II) COMPLEXES CONTAINING ISATIN / TRIPHENYLPHOSPHINE MIXED LIGANDS.

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Abstract : New cationic Fe(III),Co(II) and Ni(II) mixed ligand complexes containing both triphenylphosphine and isatin ligands were prepared and characterized using conventional physical and chemical methods of analysis, (I.R. , UV-Vis. , and ^{1}H NMR). Microanalytical data of the investigated complexes are consistent with the formulations.
$[Fe(Isa)_2\{P(Ph)_3\}_2]^{3+}$, $[Co(Isa)_2\{P(Ph)_3\}_2]^{2+}$ and $[Ni(Isa)_2\{P(Ph)_3\}_2]^{2+}$,
(Where Isa = Isatin and $P(Ph)_3$ = Triphenylphosphine).
The prepared complexes are soluble in polar solvents and could be of potential use in bio-inorganic applications.

Introduction : The coordination chemistry of iron , cobalt and nickel has attracted interest because of its possible relevance to the bio-inorganic and pharmaceutical chemistry[1].Co-cyanocobalamine for instance is used for the diagnosis of pernicious anemia and as an adjunct in the evaluation of other defects of intestinal vitamin B_{12} absorption. Nickel and its simple compounds have been the most extensively documented class of metal carcinogens in humans and therefore nickel chelators are important for nickel bio extraction. Iron is an essential component of man's biochemistry but,in common with other elements becomes toxic when in excess[2,3],and chelating agents are needed for the treatment of iron overload [2,3].

It is well established that metal chelate complexes consisting of two or more chelating agents (mixed ligand complexes) possess an additional stability over those containing just a single molecule of one of these chelating agents.This has led to the prediction that appropriate combination of chelating agents should be more effective than a single one in removing for instance certain toxic metals from mammalian body[5].In addition the extraction of some metal ions i.e.,Fe,Co and Ni from aquous solution using mixed ligand complexes lead to an increase in the percentage extraction of these metal ions[4,5].

In the present work ,we synthesized new cationic Fe(III),Co(II) and Ni(II) mixed ligand complexes containing triphenylphosphine and isatin ligands and characterized them using conventional physical and chemical methods of analysis . No previous work concerning preparation of these complexes has been described before in chemical literatures.

Experimental : All chemicals used in the present work were of A.R. grade $FeCl_3$ anhydrous, $CoCl_2$ anhydrous and $NiCl_2.6H_2O$, purchased from BDH Chemicals.Isatin and triphenylphosphine were obtained from Merck Chemicals.Acetonitrile obtained from BDH Chemicals and used without further purifications.

Synthetic manupulations were performed under argon atmosphere using standard schlenk techniques. Infra red spectra were recorded on a Perkin-Elmer model 880 spectrophotometer in the range 4000 - 200 Cm^{-1} in Kbr pellet. UV-Vis.spectra were recorded on a Pharmacia LKB biochrom 4060 spectrophotometer. ^1H nmr spectral data were obtained in acetone d_6 solvent and reported at δ value using Jeol FX - 100 spectrophotometer. Elemental analysis were obtained from Perkin-Elmer 2400 CHNSO analyser.

Preparation of $[Fe(Isa)_2\{P(Ph)_3\}_2]^{3+}$ Complex.

0.6488g.(4.0mM) of anhydrous $FeCl_3$, 2.098g.(8.0mM) of $P(Ph)_3$ and 1.177g.(8.0mM) of isatin were dissolved in 30 ml of acetonitrile under argon atmosphere, the dark brown solution was stirred for 1 hour and by slow evaporation of acetonitrile under vacuum a dark brown complex was precipitated as a product.The complex was washed with toluene and petroleum spirit. The product was stored in the argon atmosphere.

Yield : 2.97gram (3.395mM) , 85% ; M.P. 92 - 95°C .
Analytical data calculated for $[C_{52}H_{40}N_2P_2Fe]$; F.Wt. = 874.707
Calculated ; C : 71.34 % ; H : 4.57 % ; N : 3.20 % .
Found ; C : 71.41 % ; H : 4.51 % ; N : 3.42 % .

Preparation of $[Co(Isa)_2\{P(Ph)_3\}_2]^{2+}$ Complex.

0.5194g.(4.0mM) of anhydrous $CoCl_2$, 2.098g.(8.0mM) of $P(Ph)_3$ and 1.177g.(8.0mM) of isatin were dissolved in 30 ml of acetonitrile under argon atmosphere , the dark brown solution was stirred for 1 hour and by slow evaporation of acetonitrile in vacuum a dark brown product was obtained.The complex was washed with toluene and petroleum spirit . The complex was stored under argon.

Yield : 3.16 g.(3.60mM) , 90 % ; M.P. 95 - 97 °C .
Analytical data calculated for $[C_{52}H_{40}N_2O_4P_2Co]$; F.Wt. = 877.7932
Calculated ; C : 71.09 % ; H : 4.56 % ; N : 3.19 % .
Found ; C : 71.19 % ; H : 4.74 % ; N : 3.38 % .

Preparation of $[Ni(Isa)_2\{P(Ph)_3\}_2]^{2+}$ Complex.

0.9508g.(4.0mM) of $NiCl_2.6H_2O$, 2.098g.(8.0mM) of $P(Ph)_3$ and g.(8.0mM) of isatin were dissolved in 30 ml of acetonitrile under argon atmosphere ,the brown solution was stirred for 1 hour and by slow evaporation of acetonitrile in vacuum a light brown coloured complex was isolated and washed with toluene and petroleum spirit and stored under argon.

Yield : 3.054 g.(3.48mM) , 87 % ; M.P. 98 - 100 ^{0}C .
Analytical data calculated for $[C_{52}H_{40}N_2O_4P_2Ni]$; F.Wt. = 877.55
Calculated ; C : 71.10 % , H : 4.56 % , N : 3.19 % .
Found ; C : 71.30 % , H : 4.59 % , N : 3.35 % .

Result & Discussion: Metal complexation reactions were carried out according to the following equations.

$$M^{n+} + 2\,P(Ph)_3 + n\,Cl^- \rightleftharpoons [M\{P(Ph)_3\}_2]^{n+}\,[Cl]^{n-}$$

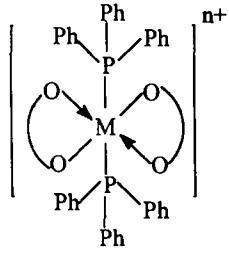
Complexation reaction

$$[M\{P(Ph)_3\}_2]^{n+}Cl^-_n + 2\,Isa \rightleftharpoons [M\{P(Ph)_3\}_2(Isa)_2]^{n+}\,[Cl]^{n-}$$

Adduct reaction

The complexes were isolated as solid products and characterised using conventional physical and chemical method of analysis . Microanalytical data of the investigated complexes were consistent with the formulation $[M\{P(Ph)_3\}_2(Isa)_2]^{n+}$. Spectral properties of the investigated complexes are tabulated in table (I) and (II).

Relevant IR bands for free isatin ligand which provide structural evidence for the mode of attachment of the ligand to the metal ions are 1740 Cm^{-1} (ν C = O) and 3191 Cm^{-1} (ν N – H) .The band at 1740 Cm^{-1} was observed at lower frequencies in the investigated complexes while the band at 3191 Cm^{-1} remained unchanged indicating that the coordination has been done via both the oxygen atoms. These results were confirmed by ^{1}H nmr spectra of the investigated complexes [table (II)] which indicate that the proton of N-H moiety in isatin was not involved in the coordination.



$M = Fe^{3+}, Co^{2+}, Ni^{2+}$
n = 3 , 2 , 2

Table 1 Some Spectral Properties of the Investigated Complexes.

Compound	IR data			U V-Vis (nm)
	ν(C=O)	ν (N-H)	ν (M-O)	λ max (ε $cm^{-1}mol^{-1}L$)
Fe $(Isatin)_2$ $\{P(Ph)_3\}_2$	1736(s)	3438(s)	505(w)	230.5($3*10^4$), 302($1.16*10^4$), 356.4($8.7*10^3$), 663..7($2*10^3$) 701($8.9*10^2$)
Co $(Isatin)_2$ $\{P(Ph)_3\}_2$	1731(s)	3411(s)	504(w)	249.5($3*10^4$), 351.5($6.3*10^3$) 400.4($4.9*10^3$), 666.5($2.6*10^3$) 699.3($1.2*10^3$),745.2($4.9*10^2$)
Ni $(Isatin)_2$ $\{P(Ph)_3\}_2$	1729(s)	3417(s)	510(w)	222.5($3*10^4$),304.3($5.4*10^3$) 394.5($1.8*10^3$),666.3($2.1*10^3$) 701($8.8*10^2$),744.6($4.3*10^2$)

Table II ^{1}H NMR Data of the Investigated Complexes.

Compound	δ (ppm)	Multi.	Int.	Assign.
$Fe(Isatin)_2\{P(Ph)_3\}_2$	8.77	s	1H	N-H
	7.77-7.06	m	12H	aromatic ring
	3.38	s	2H	$N-CH_2$
$Co(Isatin)_2\{P(Ph)_3\}_2$	8.78	s	1H	N-H
	7.77-7.06	m	12H	aromatic ring
	3.37	s	2H	$N-CH_2$
$Ni(Isatin)_2\{P(Ph)_3\}_2$	8.76	s	1H	N-H
	7.77-7.06	m	12H	aromatic ring
	3.38	s	2H	$N-CH_2$

Multi. = Multiplicity , Int.= Intensity, Assign.= Assignment.

Based on the foregoing discussion ,the above structure is plausible in which iron ,cobalt and nickel has coordination number (6) . The complexes are soluble in polar solvents and further studies concerning the applications of these complexes in bio-inorganic studies are in progress in our laboratory.

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