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Preparation, Identification and Analytical Studies of the Ligand 2-[*p*-(2´-pyrimidyl sulphamyI) phenylazo]-4,5-diphenyl imidazole (PSPAI) and Some of it's Metal Complexes

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Abstract: Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) metal complexes of new aryl azo imidazole 2-[*p*-(2´-pyrimidyl sulphamyl) phenylazo]-4,5-diphenyl imidazole (PSPAI) have been synthesized and characterized by elemental analysis, IR electronic spectra, molar conductivity measurements and magnetic moment measurements. It has been found that the azo ligand behaves as neutral bidentate (N,N´) ligand forming chelates with 1: 2 (metal : ligand) stoichiometry. The conductivity data for all complexes are consistent with those expected for an electrolyte. Octahedral environment is suggested for metal complexes.

Keywords: 2-[*p*-(2´-pyrimidyl sulphamyl) phenylazo]-4,5-diphenyl imidazole (PSPAI), Complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II), Analytical study.

الملخص: يتضمن البحث تحضير معقدات فلزية لأيونات الكوبلت (II) ، النيكل (II) ، النحاس (II) ، الخارصين (II) ، الكادميوم (II) والزئبق (II) مع الليكاند الجديدة 2-[بارا-(2´-بريمدين سلفاميل) فنيل آزو]-5،4-ثنائي فنيل إميدازول (PSPAI). شخصت الليكاند المحضرة ومعقداتها بوساطة التحليل الدقيق للعناصر والأشعة تحت الحمراء والأطياف الإلكترونية كما درست التوصيلية المولارية والخواص المغناطيسية لهذه المعقدات. لقد بينت نتائج الدراسة ان الليكاند تسلك كليكاند متعادلة ثنائية المخلب(N, N´) ترتبط مع جميع الأيونات الفلزية بنسبة مولية 1 : 2 (فلز : ليكاند).تم اقتراح الشكل ثماني السطوح لجميع المعقدات الفلزية بالاعتماد على نتائج التحاليل المذكورة.

Introduction :

A large number of (N,N´)-doner ligands in azo imine family have been prepared in the last few years [1-4]. This azo imine family contains aryl azo pyridines [5], aryl azo imidazoles [6] and aryl azo pyrimidines [7]. Aryl azo imidazoles have drawn special attention because of the synthetic simplicity of the system and the biochemical ubiquity of imidazole [8]. This type of molecules has several advantages. They are used as analytical reagents [9,10], and as a staining agents [11]. This class of azo compounds possess active (π-acidic) azo imine (─N═N─C═N─), function and efficient agents to stabilities low valent metal oxidation states [12,13], due to the presence of azo-centered π*-molecular orbital, for this reason a number of these azo compounds were synthesized and their abilities as chelating ligands [13-15] was investigated.

The present study reports the synthesis and characterization of new azo imidazole ligand (PSPAI), and some of it's metal complexes.

Experimental

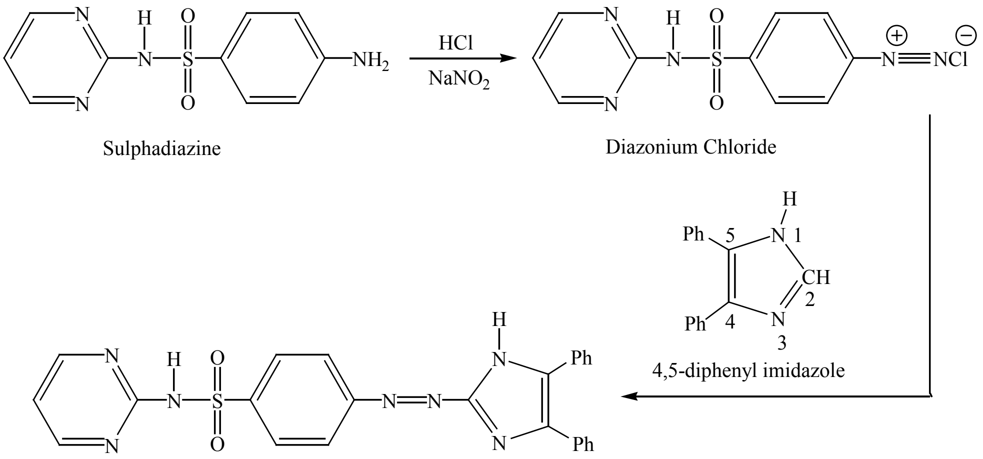
Materials and measurements

All reagents and solvents were obtained from commercial sources and used as received, except of 4,5-diphenyl imidazole was prepared as reported procedure [16]. Elemental analyses were carried out by means of Micro analytical unit of 1108 C.H.N Elemental analyzer. IR spectra were recorded using KBr discs 4000-400 cm^{-1}on FT-IR Testscan Shimadzu model 8000. UV - Vis. Spectra were recorded in ethanol on Shimadzu model 1700 UV-Vis Spectrophotometer . Magnetic susceptibilities were measured as powder samples using Faraday method, Balance Magnetic MSB-MKI was employed for this purpose. The diamagnetic corrections were made by Pascal's constants. The metal content of the complexes was measured using atomic absorption technique by Shimadzu (AA-160). Molar conductance measurements were determine in DMF by using a Alpha Digital conductivity meter model 800. pH measurements were carried out using WTW pH meter model 720. Electro Thermal malting point model 9300 was used to measure the melting points of the ligand and it's complexes.

Preparation of the ligand (PSPAI)

(PSPAI) ligand was prepared according to the following general procedure [17] (Scheme 1). *P*-(2-pyrimidyl sulphamyl) aniline (2.5 g, 10 mmol) was dissolved in 30 ml of water and 6 ml of concentrated hydrochloric acid. The filtered solution was diazotized below 5°C with 15 ml of aqueous (1.0 M) sodium nitrite. The resulting diazonium chloride solution was mixed with 4,5-diphenyl imidazole (2.2 g, 10 mmol) dissolved in 200 ml alkaline ethanol cooled below 0°C. After leaving in the refrigerator for 24 hr, the mixture was acidified with dilute hydrochloric acid until pH = 5. The precipitate was filtered off, and recrystallized twice from hot ethanol, and dried in a vacuum desicator .

Preparation, Identification and Analytical Studies



Scheme.1: Preparation of the (PSPAI) ligand

Preparation of complexes

The complexes were prepared by dissolving (0.481g, 1mmol) of ligand in 50 ml of ethanol which then added dropwise with vigorous stirring to (0.5mmol) of MCL_2 salts [M= Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)] dissolved in 10 ml hot distilled water. The mixture was heated to 50°C for 30 min, then left over night. The solid complex formed was filtered , washed with 5 ml hot ethanol and dried in a desicator over anhydrous $CaCl_2$.

Results and discussion

Characterization of ligand and its metal complexes

The azo ligand was orange crystals, but the chelat complexes of this ligand vary in color from red to purple. The ligand and it's complexes were insoluble in water but soluble in most organic solvents. The elemental analysis are in agreement with the formulae of the ligand and it's complexes given in Table1.

Table 1: Analytical and physical data of the (PSPAI) ligand and it's complexes

No	Compound (Color)	Formula Mp (Yield)	Found (Calcd)			
			C	H	N	M
1	L=(PSPAI) (Orange)	$C_{25}H_{19}N_7O_2S$ 274-276 (72%)	62.23 (62.37)	3.86 (3.95)	20.41 (20.37)	-----
2	[Co L_2Cl_2] (Brawn)	$C_{50}H_{38}N_{14}O_4S_2Cl_2Co$ 238-240 (75%)	54.78 (54.94)	3.39 (3.48)	17.78 (17.94)	5.01 (5.39)
3	[Ni L_2Cl_2] (Dark brawn)	$C_{50}H_{38}N_{14}O_4S_2Cl_2Ni$ 278-280 (69%)	54.73 (54.96)	3.32 (3.48)	18.17 (17.95)	5.11 (5.37)
4	[Cu L_2Cl_2] (Green-violet)	$C_{50}H_{38}N_{14}O_4S_2Cl_2Cu$ 207-209 (70%)	54.92 (54.73)	3.51 (3.46)	17.65 (17.87)	5.46 (5.79)
5	[Zn L_2Cl_2] (Brawn)	$C_{50}H_{38}N_{14}O_4S_2Cl_2Zn$ 241-243 (68%)	54.83 (54.62)	3.24 (3.46)	18.01 (17.84)	5.61 (5.95)
6	[Cd L_2Cl_2] (Red)	$C_{50}H_{38}N_{14}O_4S_2Cl_2Cd$ 258-260 (69%)	52.52 (52.38)	3.18 (3.31)	17.26 (17.11)	9.43 (9.81)
7	[Hg L_2Cl_2] (Dark red)	$C_{50}H_{38}N_{14}O_4S_2Cl_2Hg$ 217-219 (65%)	48.39 (48.63)	2.86 (3.08)	15.73 (15.88)	------

Metal : ligand ratio

The (metal : ligand) ratios of complexes were determined by molar ratio method at fixed concentration and pH at wavelengths of maximum absorption. The results are given in Table 2, the ligand was found to form (2 : 1) chelates with all metal ions, these results are in agreement with the values reported for some aryl azo imidazole complexes [18,19].

Table 2: Metal : Ligand ratios determination by the method of mole ratio and the calculated Stability constant values

Ligand	Metal ion	pH	λ_{max} nm	Metal : Ligand	β	Log β
(PSPAI)	Co(II)	8.0	615	1 : 2	2.873×10^{10}	10.45
	Ni(II)	6.0	599	1 : 2	3.965×10^{10}	10.59
	Cu(II)	6.0	633	1 : 2	13.663×10^{10}	11.13
	Zn(II)	9.0	512	1 : 2	2.293×10^{10}	10.36
	Cd(II)	8.0	514	1 : 2	1.093×10^{10}	10.03
	Hg(II)	9.0	524	1 : 2	9.71×10^{9}	9.98

Calculation of the metal complexes stability constant

Stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength λ_{max} and pH values. The degree of formation of the complexes is obtained according to the relationship [20], $\beta = (1 - \alpha) / (4\alpha^3c^2)$, and $\alpha = (A_m - A_s)/A_m$, where A_s and A_m are the absorbance's of the partially and fully formed complex respectively at optimum concentration.

The calculated β and Log β values for the prepared complexes are recorded in Table 2, the stability follows the sequence; Co(II) < Ni(II) < Cu(II) > Zn(II) > Cd(II) > Hg(II), the sequence of metal ions of the first row transition metal agree with Irving-Williams series of stability constant [21].

Infrared spectra

Selected IR absorption of ligand and its complexes are given in Table 3. The medium and broad band at 3380 cm^{-1} in the spectrum of the ligand may be attributed to the ν(N─H) of imidazole ring [26]. This band remains in the same region in free ligand and in complexation. Thus, the remaining of amine hydrogen group intact in solid complexes indicats its non involvement in coordination of the ligand to the metal ions [22].

The spectrum of the ligand shows absorption band at 1585 cm^{-1} due to ν(C═N) of the N_3 imidazole nitrogen. It is observed with a little change in shape and shifted to lower frequencies 1580 – 1570 cm^{-1} in the prepared complexes spectra. These differences suggest the linkage of metal ion with nitrogen imidazole ring [23].

The ν(N═N) stretching vibration appears at 1440 cm^{-1} in the free ligand spectra. This band appearing at 1420 – 1405 cm^{-1} with different in shape and reduced in intensity in the spectra of complexes. Both band shifted and reduced intensity due to complex formation [24,25].

The spectrum of free ligand show two absorption bands at 1350 and 1170 cm^{-1} due to symmetrical and asymmetrical vibration of ν(O═S═O) group [26]. These bands are stable in position and intensity in both ligand and its metal complexes.

New weak bands in the region 460 - 415 cm^{-1} were observed in the spectra of metal complexes. These bands were not present in the spectrum of legend, and they due to ν(M─N) [27].

Thus the above IR spectra data lead to suggest that the ligand behaves as a bidentate chelating agent, and the coordination sites are, the nitrogen atom of azo group nearest to a phenyl ring, and N3 atom of the imidazole ring, to give five-membered chelat ring.

Table 3: Characteristic IR absorption bands of the ligand and it's complexes in cm^{-1} units

Compd.	ν (N–H)	ν (C– H) Ar.	ν (C=N)	ν (N=N)	ν (O=S= O)	Imi.r.de	ν (M–N)
(PSPAI)	3400 mbr	3080 w	1585 s	1440 m	1350m 1170s	1060w	------
[Co L_2Cl_2]	3400 wbr	3080 w	1580 m	1410 m	1350w 1170w	1060 w	420w
[Ni L_2Cl_2]	3400 wbr	3080 w	1580 m	1420 s	1350w 1170s	1060m	415w
[Cu L_2Cl_2]	3400 w	3075 w	1580 s	1410 m	1345w 1160s	1060m	445w
[Zn L_2Cl_2]	3400 w	3080 w	1570 m	1410 s	1350m 1170s	1060 w	455 w
[Cd L_2Cl_2]	3400 wbr	3080 w	1575 m	1410 s	1350m 1165s	1060 w	460 w
[Hg L_2Cl_2]	3400 wbr	3080 w	1575 m	1405 s	1345m 1165s	1060 w	425 w

L = ligand, s = strong, w = weak, m = medium, br = broad.

Magnetic measurement and Electronic spectra

The spectral data and the magnetic moment of prepared complexes are listed in Table 4. The magnetic moment of the Cobalt (II) has been found to be (4.46 B.M), which is with the range of octahedral Cobalt (II) complexes [28]. The electronic spectra of this complex shows three absorption bands at 14650, 16430 and 23860 cm^{-1}, there are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_1(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(p)(\nu_3)$ transitions, respectively, which are characteristic of octahedral stereo chemistry(29). For the Nickel (II) complex, its magnetic moment (3.10 B.M), and d–d spectrum of this complex show bands at 14280 and 22380 cm^{-1}, which are suggesting the existence of $^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(p)(\nu_3)$ transitions with an octahedral spatial configuration [29].

The magnetic moment value of the copper (II) complex (1.71 B.M) which may suggest an octahedral structure. It's electronic spectrum shows a band centered at 15610 cm^{-1} which may assigned to $^2E_{2g} \rightarrow {}^2T_{2g}$ transition in octahedral environment [28]. zinc (II), cadmium (II) and mercury (II) complexes are diamagnetic and the electronic spectra of there complexes exhibit high intense charge transfer transition in the visible region (512-524 nm) which are assigned to (MLCT) [30].

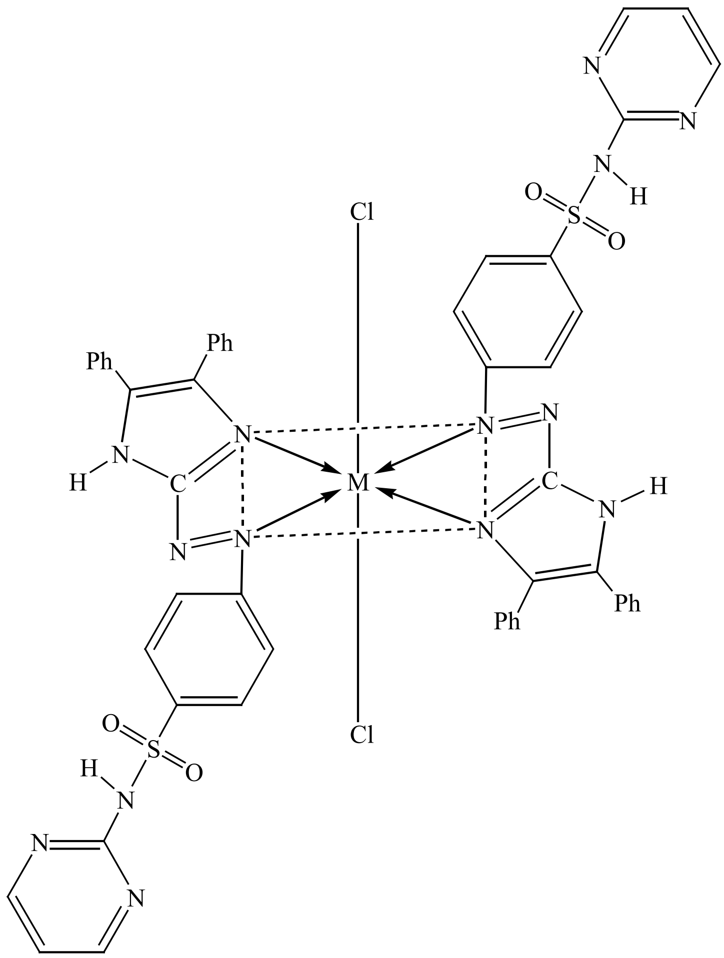
Table 4: Electronic spectra, conductivity and magnetic moment of chelate complexes

Complex	Absorption bands (cm^{-1})	Transition	Conductivity $S.mol^{-1}.cm^2$	μ_{eff} (B.M)
[Co L_2Cl_2]	14650 16430 23860	${}^4T_1g(F) \rightarrow {}^4T_2g(F)V_1$ ${}^4T_1g(F) \rightarrow {}^4A_2g(F)V_2$ ${}^4T_1g(F) \rightarrow {}^4T_1g(P)V_3$	8.12	4.46
[Ni L_2Cl_2]	14280 22380	${}^3A_2g \rightarrow {}^3T_1g(F)V_2$ ${}^3A_2g \rightarrow {}^3T_1g(P)V_3$	9.85	3.10
[Cu L_2Cl_2]	15610	${}^2E_2g \rightarrow {}^2T_2g$	11.72	1.71
[Zn L_2Cl_2]	------	------	10.97	dia
[Cd L_2Cl_2]	------	------	12.19	dia
[Hg L_2Cl_2]	------	------	12.43	dia

Conductivity measurements

The complexes are non- electrolytes as shown by their conductivity in DMF at room temperature [31], The values are in the range 8.12- 12.43 S mol^{-1} cm^2. (Table4)

According to these results the structural formula of prepared complexes may be proposed in Fig.1.



M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)

Fig.1: The proposed structural formula of the metal complexes

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