



Synthesis, spectroscopic and Kinetic studies of some N-aryl pyridinium derivatives

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ABSTRACT

New N- phenylpyridinium derivatives compounds were synthesized, their molecule structure were confirmed by elemental analyses, IR, NMR and UV-visible spectroscopy. The reaction kinetics of these compounds with metal ions such as Fe²⁺, Cu²⁺ and V³⁺ were investigated by conductivity and spectroscopy methods respectively at different time and different temperature. From spectroscopy and conductivity studies of N-phenylpyridinium compounds under investigation we found the values of activation energy for all compounds in conductometric methods (1.7-9.2 kJmol⁻¹) are smaller than the corresponding values measured by spectroscopy method (2.2-13.5 kJ mol⁻¹), therefore we can conclude that the conductometric methods is better than spectroscopy method for studying kinetic reaction for these compounds.

Key word: N- phenylpyridinium, reaction kinetics, conductivity and spectroscopy methods

INTRODUCTION

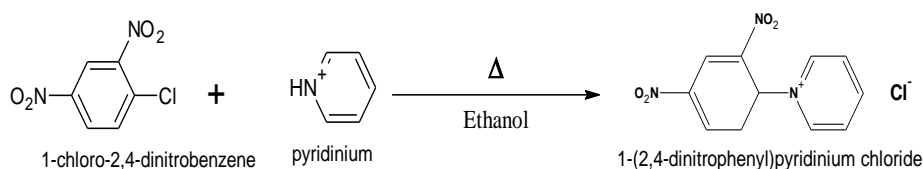
Pyridinium salts are a versatile class of compounds used as phase transfer catalysts [1], initiators of cationic polymerization[2] antimicrobials, cationic surfactants [3], enzyme inhibitor [4], acylating agents[5] and dyes. Pyridinium salts contained a chiral auxiliary group linked to the ring nitrogen. Schiff bases Synthesis of (2-Chloropyridine-3-yl)-(4-nitrobenzylidene) amine and its antibacterial activity were reported to show a variety of biological activities such as antibacterial [6], antifungal [7,8], anticancer [9,10] and herbicidal activities[11]. Pyridinium compounds have biological activities [12] such as antifungal [13] and antibacterial activities [14]. Ballardini *et.al.* examined compounds bearing either alkyl or aryl substituents on the quaternarized nitrogen atoms, showed that their spectroscopic and electrochemical properties were fine-tuned by the nature of the substituents and found that the photophysical, photochemical and electrochemical properties of such compounds are not only determined by the structure of the N-heterocyclic central moiety, but are also remarkably affected by the peripheral substituent's linked to the quaternarized nitrogen atoms. In all cases, the presence of the benzyl substituents renders easier the electrochemical reduction of

these compounds, owing to an increased delocalization of the added electron(s). These results can be helpful in the design of functional molecular and supramolecular systems and materials that make use of such electron-accepting moieties[15]. A general method for estimating reaction rate constants of chemical reactions using ultraviolet-visible (UV-vis.) spectroscopy is presented. The only requirement is that some of the chemical components involved be spectroscopically active[16]. The reaction rate constants and the individual spectra of the reacting absorbing species of the two-step consecutive reaction of 3-chlorophenylhydrazonopropane dinitrile with 2-mercaptoethanol were estimated simultaneously from UV-vis. recorded spectra in time. The results obtained were excellent[17].

EXPERIMENTAL

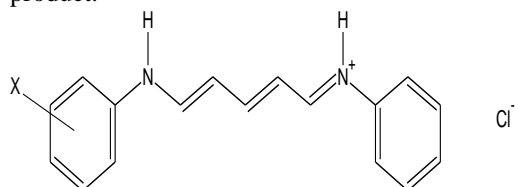
Preparation of N-2,4-dinitrophenylpyridinium chloride: Pyridine (5.0g, 0.063 moles) and 1-chloro-2, 4-dinitrobenzene (13.0g, 0.064 moles) were refluxed in ethanol (20 ml) for 4 hours. The cold solution was then treated with excess ether to give a white precipitate of N-2,4- dinitro phenyl pyridinium chloride. The product was filtered, washed several times with ether.

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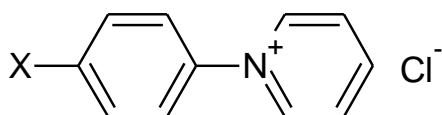
Preparation of some derivative N-phenylpyridinium chloride:

N-2,4-dinitrophenylpyridinium chloride (10.0g) in ethanol (20 ml) was added to a stirred solution of a(2moles)X (where X is aniline, *p*-toluidine, *p*-aminobenzoic acid, *p*-aminophenol and *p*-chloroaniline) in the same solvent (10 ml) to give a dark red precipitate of 5-anilino N-phenyl-2,4-pentadienylideneiminium chloride. After 30 minutes, the product was filtered then washed thoroughly with acetone to remove any dinitroaniline residue which could be mixed the product.



5-anilinoN-phenyl-2,4-penta-dienylideneiminium chloride

To a solution of 5-anilinoN-phenyl-2,4-penta-dienylideneiminium chloride (6.0 g) in methanol (300 ml) triethylamine (3 ml) was added and the mixture was refluxed at 50 (- 55 °C) for 24 hours. The solvent was then evaporated in rotary evaporator to leave a hygroscopic product of N-phenylpyridinium chloride which was washed with acetone and ether to remove any residue of aniline formed during the cyclization (hygroscopic product).



Where: X = -H, N-phenylpyridinium chloride (A); -CH₃, N-(*p*-methylphenyl) pyridinium chloride (B); -COOH, N-(*p*-carboxyphenyl) pyridinium chloride (C) and -OH, N-(*p*-hydroxyphenyl) pyridinium chloride (D)

Conductivity Measurement: The conductivities of the compounds were determined by dissolving the appropriate weight in ethanol with $4 \times 10^{-5} \text{M}$ and $1 \times 10^{-3} \text{M}$ for metal ions (Cu^{2+} , Fe^{2+} and V^{3+}) dissolving in distilled water. The conductivity of a known volume of a compound solution is measured without addition of metal ion solution. Then in each run different volume of metal ion were added (ml) at different time interval. The experiment was carried out at 20, 25, 35 and 45°C. The measurements were carried out using a conductance bridge; the type of conductance was AP75; conductivity TDS meter, Fisher Scientific and the type of water bath was Iso. Temp 110, Fisher Scientific.

RESULTS AND DISCUSSIONS

Spectroscopic studies for Molecular Structure investigation:

The prepared compounds were investigated by spectroscopic techniques such as Infrared (IR) and nuclear magnetic resonance (¹H-NMR). The Infrared spectra (IR) of all compounds and their metal chelates showed $\nu\text{-C}=\text{C}$ stretching bands of an aromatic ring of pyridinium around 1473, 1625 cm^{-1} . While $\nu\text{-CH}$ stretching appeared in the position 3032-3070 cm^{-1} . The out of plane $\nu\text{-CH}$ bending appeared at 760-850 cm^{-1} for all compounds. The band at 1251.7 to 1357.8 cm^{-1} was assigned to $\nu\text{-C-N}$ which appeared in the spectra of all compounds. $\nu\text{-OH}$ strong band between 2500-3310 cm^{-1} appeared in compounds C and D respectively. $\nu\text{-C-O}$ bands appeared in range 1378-1372 cm^{-1} for compounds C, D while $\nu\text{-C=O}$ band appeared at 1558 cm^{-1} for compound D (table 1). ¹H-NMR of all compounds under study showed doublet peak at range between (8.9-9.2 ppm) and triplet peak in at 8.1 ppm in the range between 8.5-8.6 ppm all these positions represented for pyridinium ring protons. For compounds A, B and E singlet peak appeared at the range (7.5 to 7.6 ppm) which assigned for phenyl ring protons in compounds C and D respectively (table 2). The IR and NMR of the compounds are provided in the supplementary material.

Table (1): IR spectra for compounds (A, B, C, D and E)

Compound s	ν C=C cm^{-1}	ν =CH(st) cm^{-1}	=C-H(ben.) cm^{-1} ν	ν C-N cm^{-1}	ν -OH cm^{-1}	ν C=O cm^{-1}	ν C-O cm^{-1}
A	1473.3,1625.4	3048	681.7,762.6	1254.4	-		
B	1477.7, 1639.6	3051.6	775.2	1251.1	-		
C	1474, 1558.3	3070.6	771.3	1378.3	2500.6-3310	1558.3	1378.3
D	1474,1600.8	3048.8	843.5	1249.5	3310.2		1372.7
E	1478.3, 1630.4	3032.7	839.9	1259.2	-		

Table 2: $^1\text{H-NMR}$ spectra for compounds(A,B,C,D and E)

compounds	δ H _{1,5}	δ H _{2,4}	δ H ₃	δ H _{11,9}	δ H _{8,12}
A	9.02 ppm	8.18 ppm	8.65 ppm	7.6608ppm	7.6608ppm
B	9.0 ppm	8.15ppm	8.61ppm	7.5 ppm	7.5 ppm
C	9.1 ppm	8.15 ppm	8.65 ppm	8 ppm	7.65 ppm
D	8.9 ppm	8.1 ppm	8.55 ppm	6.99 ppm	7.5 ppm
E	9.01 ppm	8.15 ppm	8.65 ppm	7.66 ppm	7.66 ppm

Determination rate constant of N-phenyl pyridinium derivative compounds by Spectroscopic studies: The reaction rates were followed by spectrophotometric method, all reaction was done under first order conditions in which the concentration of the Pyridinium compounds were at least 10 times as large as that of metal ions (Cu^{2+} , V^{3+} , Fe^{2+}). The concentration of the Pyridinium compounds were 1×10^{-4} M whereas that of metal ions 1×10^{-3} M. All reactions were done at four temperatures (25, 35, 45, and 50 °C). The kinetic experiment was initiated by the addition of 2.5 ml from each solution in a 25 ml flask and completed with ethanol (Start the stop watch at the time of the first addition). And thermostated at the desired temperature. The mixed reaction is transferred to the spectrophotometer quartz cell, placed in cell holder and the experiment started. Initially as well as in a number of experiments full spectral scans between $\lambda=500$ nm and $\lambda=200$ nm were done. The absorption spectra of all compounds in ethanol shows band at range 260-261 nm with different metal ions while the compound D has another band at 317 nm (fig.1).

The integrated rate law for a first -order reaction can be written in the form:

$$\ln\left(\frac{P_t - P_\infty}{P_0 - P_\infty}\right) = -kt$$

Where: P_0 , P_t and P_∞ are absorbance values of the solution at time zero, t and ∞ respectively.

From Table (3) the value of rate constant of reaction at different temperature, we observe there are different values of k for all compounds with different metal ions are increased with temperature increasing, the smaller value of k appears in a compound D with Cu^{2+} ion. The activation energy which is calculated from Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT}$$

Where: A, E_a and k are pre-exponential factor, the Arrhenius activation energy and rate constant respectively, R and T are gas constant and temperature, a plot of $\ln k$ vs. $1/T$, should give a straight line with slope = $-E_a/R$ (E_a kJ. mol^{-1}). The greatest value of E_a appear in compound B (135.4 kJmol^{-1}) with Cu^{2+} ion this can be explained that copper ion (Cu^{2+}) has a smallest ionic radius (72pm), and due to steric hindrance of compound B, while smallest value of activation energy were recorded for a compound A. The activation energy of compound B with V^{3+} ($85.6448 \text{ kJmol}^{-1}$) while for compounds A, D and C ($84.09, 51.5$ and 21.1 kJ mol^{-1}) compared with that for a compound B this is due to large ionic radius of V^{3+} (78 pm) and also the nature of substitute function groups of compound. The activation parameters such as free energy change (ΔG), entropy (ΔH), entropy (ΔS)

and activation energy (E_a) for the reaction under study were calculated using equations:

$$\Delta S = \left[\ln \frac{Ah}{kT} \right] R$$

$$\Delta H = E_a - RT$$

$$\Delta G = \Delta H - T\Delta S$$

Where: K , h and R are Boltzmann and Plank constants and gas constant respectively. From table (4), the values of entropy (ΔS) were different in all compounds with metal ions. The positive values of enthalpy ΔH are due to endothermic reactions. The values of free energy ΔG were positive in all compounds with metal ions except compound A with Cu^{2+} , so the reaction in all compounds with metal ions non-spontaneous except A with Cu^{2+} was spontaneous.

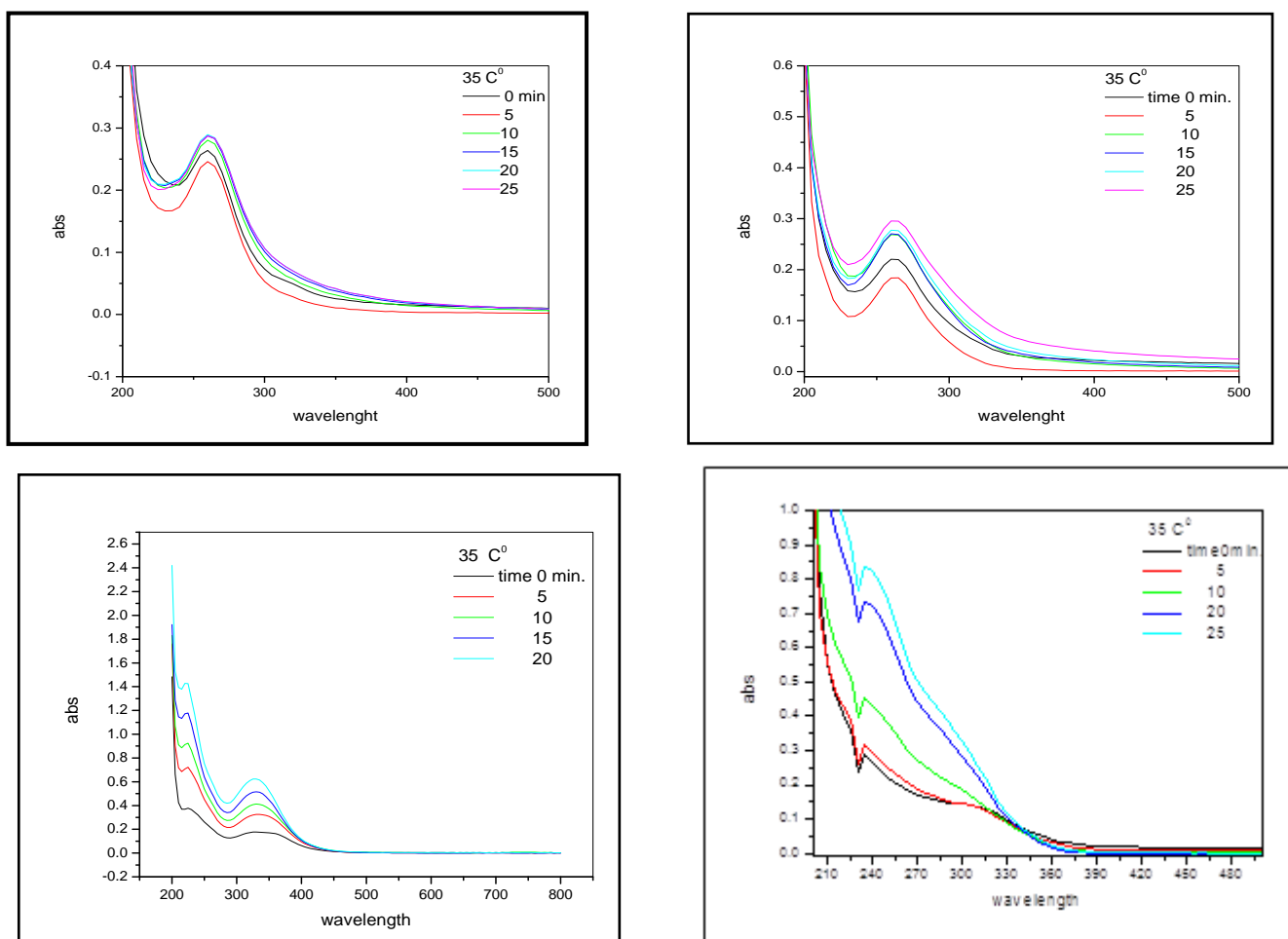


Fig (1) :Effect of time and temperature on the absorption spectra for compounds A and B with copper ions (Cu^{2+}) and D with iron ions (Fe^{+2}) and Vanadium ions (V^{+3}) respectively

Table 3: Rate constant and activation energy for all compounds from Spectroscopic studies

Parameter	Cu ²⁺ (72pm)			V ³⁺ (78pm)			Fe ²⁺ (77pm)		
	K (s ⁻¹)	E _a (kJ mol ⁻¹)	A(s ⁻¹)	K (s ⁻¹)	E _a (kJ mol ⁻¹)	A(s ⁻¹)	K (s ⁻¹)	E _a (kJ mol ⁻¹)	A(s ⁻¹)
TC°	A-(-H)								
25C°	0.541	3.105	1.893	0.049	8.4096	2.678x10 ¹³	-	-	-
35C°	0.548			0.148			-	-	-
45C°	0.561			0.417			-	-	-
50C°	0.591			1.99			-	-	-
B-(P-CH ₃)									
25C°	0.0105	13.549	5.75 x10 ²¹	0.048	8.5645	4.876x10 ¹³	-	-	-
35C°	0.0621			0.1478			-	-	-
45C°	0.3708			0.4229			-	-	-
50 C°	1.55			1.1344			-	-	-
C-(P-COOH)									
25C°	0.0475	3.3796	3.9682x10 ⁴	0.1273	2.1498	646.388			
35C°	0.0740			0.1679			-	-	-
45C°	0.1121			0.2177			-	-	-
50C°	0.665			0.2778			-	-	-
D-(P-OH)									
25C°	1.793	2.117	1.092x10 ³	0.056	6..5413	60.11x10 ⁵	0.0524		272.58
35C°	2.476			0.110			0.0692		
45C°	3.223			0.207			0.0897		
50C°	4.2075			0.375			0.1146		

Table 4: The thermodynamic parameters for all compounds from Spectroscopic studies

Compounds	Cu ²⁺			V ³⁺		
	ΔS JK ⁻¹ mol ⁻¹	ΔH Jmol ⁻¹	ΔG Jmol ⁻¹	ΔS JK ⁻¹ mol ⁻¹	ΔH Jmol ⁻¹	ΔG Jmol ⁻¹
A	181.55	2.8575x10 ⁴	-2.5350 x10 ⁴	12.147	8.1617x10 ⁴	7.7995x10 ⁴
B	171.65	13.301x10 ⁴	8.1832 x10 ⁴	17.1306	8.3165x10 ⁴	7.8058x10 ⁴
C	-176.019	3.132x10 ⁴	8.3797x10 ⁴	-191.107	1.8670x10 ⁴	7.5649x10 ⁴
D	-186.74	2.064x10 ⁴	7.6315x10 ⁴	-115.1362	4.9062x10 ⁴	8.3390x10 ⁴
D (Fe ²⁺)	-217.42	1.873x10 ⁴	8.356x10 ⁴			

Table 5: Rate constant and activation energy for all compounds from by Conductometric methods

Parameter	Cu ²⁺ (72pm)			Fe ²⁺ (77pm)			V ³⁺ (78pm)		
	K x10 ⁻⁴ (s ⁻¹)	E _a (kJ mol ⁻¹)	A(S ⁻¹)	K x10 ⁻⁴ (s ⁻¹)	E _a (kJ mol ⁻¹)	A(S ⁻¹)	K x10 ⁻⁴ (s ⁻¹)	E _a (kJ mol ⁻¹)	A(S ⁻¹)
C ^o	A-(H)								
20C ^o	5.0022	7.94277	0.01316	6.2960	1.75042	0.8488	9.7575592	7.75446	0.0237
25C ^o	5.3425			7.27871			10.405028		
35C ^o	5.9279			9.153291			11.516809		
45C ^o	6.53466			11.3460			12.66629		
B-(P-CH ₃)									
20C ^o		4.5140	4.112x10 ⁻³	11.87201	3.7891	5.649x10 ⁻³	11.52325	1.0034	1.741x10 ⁻³
25C ^o	6.6564797			12.25063			11.61853		
35C ^o	7.061703			12.87365			11.77216		
45C ^o	7.46381			13.48624			11.91799		
C-(P-COOH)									
20C ^o	5.351086	9.0719	0.0224	9.64866	5.6432	9.851x10 ⁻³	10.60197	4.1827	5.932x10 ⁻³
25C ^o	5.768786			10.11050			10.97582		
35C ^o	6.496266			10.8857			11.59360		
45C ^o	7.261071			11.6661			12.20408		
D-(P-OH)									
20C ^o	4.784557	5.3660	4.358x10 ⁻³	8.390535	7.8409	0.0211	10.85602	9.2218	0.04836
25C ^o	5.00207			8.953705			11.71799		
35C ^o	5.366101			9.921636			13.22163		
45C ^o	5.731259			10.92348			14.80543		

Table 6: The Thermodynamic parameters of Compounds by Conductometric methods

Parameter	Cu ²⁺ (72pm)			Fe ²⁺ (77pm)			V ³⁺ (78pm)		
	ΔG (kJmol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	ΔG (kJmol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)	ΔG (kJmol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (JK ⁻¹ mol ⁻¹)
A-(H)	89.20339	5.44888	-280.91471	72.6985	-0.728x10 ³	-246.27	5.55166	5.22756	-276.023
B-(P-CH ₃)	88.6734	2.03518	-290.586	86.26687	1.31028	-284.945	87.29325	1.4754	-297.7316
C-(P-COOH)	89.02934	6.59308	-276.4926	87.64985	3.16438	-283.365	87.44718	1.70388	-287.584
D-(P-OH)	89.38133	2.88718	-290.109	87.946	5.36208	-276.989	87.27461	6.74298	-270.1048

Determination rate constant of N-phenylpyridinium derivative compounds by conductivity studies: The N- phenylpyridinium derivative compound were reacted with metal ions (Cu^{2+} , Fe^{2+} , V^{3+}) at different temperature (20, 25, 35, 45 $^{\circ}\text{C}$), and conductivity was measured at different time for every temperature.

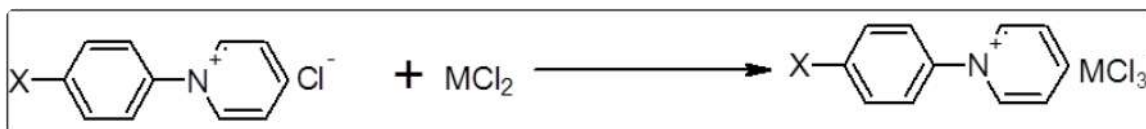
$$\ln \frac{(C_{\infty} - C_t)}{C_{\infty}} = -Kt$$

Where, C_t , C_{∞} are the conductance of the solution at time t and ∞ respectively .A plot of $\ln [(C_{\infty}-C_t)/ C_{\infty}]$ vs. time for each temperature should give a straight line with slope of $-k$. The value of conductivity increased with time and add (ml) of metal ions in all compounds. Table (5) shows the value of rate constant of reaction k at different temperature. the values of k in all compounds with Cu^{2+} were the smallest and the largest with V^{3+} the smallest value of k appear at compound D with Cu^{2+} and Fe^{2+} while it has the largest value with V^{3+} . The greatest value of E_a appear for compound C (9.0719 kJ mol^{-1}). From the table (6) the entropy (ΔS) values were

different between one compounds to another, all compounds have a negative value. The values of enthalpy (ΔH) gave a positive value for all compounds, so the reaction was endothermic while compound A with Fe^{2+} gave a negative value so the reaction was exothermic. The values of free energy ΔG positive in all compounds with metal ions this indicated the reaction for all compounds with metal ions were non-spontaneous.

CONCLUSION

From spectroscopy and conductivity studies of N-phenylpyridinium compounds under investigation we found the values of activation energy for all compounds in conductometric methods (1.7-9.2 kJ mol^{-1}) are smaller than the corresponding values measured by spectroscopy method (2.2-13.5 kJ mol^{-1}), therefore we can say that the conductometric methods is better than spectroscopy method for studying kinetic reaction for these compounds. Therefore the proposed mechanism for the reaction between N-phenylpyridinium compounds and metal ions as following



Where X: H, $-\text{CH}_3$, $-\text{COOH}$ and $-\text{OH}$ and M: Fe^{2+} , V^{3+} and Cu^{2+}

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