Qualitative Studies of Reactions of New Organic Reagents Towards Some Metal Ions.

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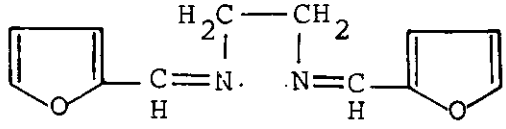
Summary: The new organic reagents, bis(furfural) ethylenediimine, 2,3-bis(2-furyl)-5,6-dihydropyrazine and 2,3-bis(2-furyl) pyrazine have been prepared by simple synthetic routine. The reagents are characterized with the aid of I.R., U.V and mass spectrometry. The reactions of the reagents towards Cu(II), Cu(I), Fe(II), Fe(III), Co(II), Ni(II) have been studied spectrophotometrically. The molar absorptivities at their λ-max are reported. The complexes are weakly coloured and rate of complex formation is slow. The complexes failed to extract in chloroform.

Pyridyl-substituted pyrazines and quinoxalines containing ferroin, cuproin and terrion reactive atmoic groupings have attracted the interests because of their close resemblance to 1,10-phenanthroline and 2,2-bipyridine[1,2,3]. They form highly coloured complexes with iron(II) and copper(I) to enable their determinations spectrophotometrically at low concentrations involving a fewer interferences [4,5,6]

It was therefore considered worth-while to prepare probable bidentate and tetradentate ligands, 2,3-bis(2-furyl)-5,6-dihydropyrazine(II), 2,3-bis(2-furyl)pyrazine (III), and bis (furfural) ethylenediimine(I) to investigate the effect of replacement of pyridyl group with nonbasic furyl group in dihydropyrazine and pyrazine rings, and bis(pyridinal) ethylenediimine[7] on the colour reactions towards metal ions.



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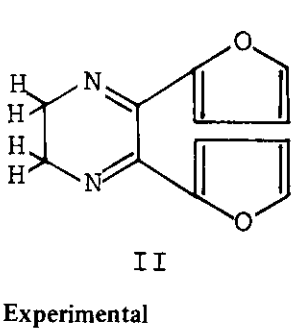

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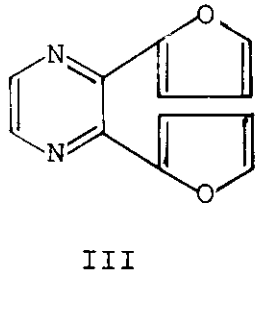

III

Experimental

Preparation of Reagents:

Bis(furfural) ethylenediimine. Ethyldiamine (3 ml) dissolved in 5 ml of ethanol was slowly added to the freshly distilled furfural (10 ml) in 15 ml of ethanol. The reaction mixture was kept cool and solvent was allowed to evaporate at room temperature. The brown semi gummy mass was extracted several times with petroleum ether (40 to 60°). The light coloured solid so obtained was recrystallised twice from petroleum ether (40 – 60°) to obtain colourless product melting at 51°C. $C_{12}H_{12}N_2O_2$ requires % C = 66.6, H = 5.5, N= 19.9; found % C = 66.66, H = 5.72, N = 12.99. The compound develops brown colour slowly on keeping at room temperature (35°). I. R. spectrum in KBr shows the bands at 3120, 3080, 2900, 2860, 2840 cm^{-1} for ν C-H; 1645 cm^{-1} for ν C=N; 1565, 1480, 1390 cm^{-1} for ν ring; 1460 cm^{-1} for δ-CH_2 and at 930, 900, 882, 850, 820, 780, 765 cm^{-1} for γ C-H vibrations. Mass spectrum shows m/e at 216(13.6%) corresponding to the molecular ion. Other main peaks are at m/e 123(93.6%), 108(100%), 95(30%), 81(44.5%) and at 67(55%).

2,3-Bis(2(furyl)-5,6-dihydropyrazine. Freshly distilled furfural in the presence of potassium cyanide was condensed to furoin, which was oxidized with copper sulphate and pyridine to α,α-diketone, furil by a reported method[8].

Ethylenediamine (1.2 ml) dissolved in ethanol (5 ml) was slowly added to the refluxing solution of furil (3.8 g) in 20 ml of ethanol. The solution was heated for 10 minutes and solvent was allowed to evaporate at room temperature. The brown mass obtained was extracted several times with ether and equal amount of petroleum ether (40-60°) was added. The precipitate obtained by partial evaporation of the solvent was twice recrystallized from petroleum

ether (40-60°) melting at 122°C. $C_{12}H_{10}N_2O_2$ requires % C = 67.80, H = 4.67, N = 13.08; found % C = 67.32, H = 4.84, N = 13.09. I. R. spectrum in KBr shows the bands at 3140, 2950 cm^{-1} for νC-H; at 1660 cm^{-1} for ν C=N dihydropyrazine ring at 1595, 1535, 1490, 1380 cm^{-1} for ν rings; at 1448 cm^{-1} δ CH_2 of dihydropyrazine ring and at 935, 890, 868, 840, 822, 770 cm^{-1} for γ C-H vibrations. Mass spectra shows m/e at 214 (30%) corresponding to he molecular ion. Other main peaks are at m/e 185(8.2%), 121(2.7%), 107(2.7%), 93(100%).

2,3-Bis (2-furyl) pyrazine. 2,3-Bis(2-furyl)-5,6-dihydropyrazine (1.0 g) dissolved in mesitylene (10 ml) was added palladium charcoal (10 %, Pd) (0.1 g). The mixture was heated for 36 hours and was filtered while hot. The solvent was allowed to evaporate at room temperature and the residue was extracted several times with ether and equal amount of petroleum ether (40-60°) was added. Yellow coloured solid obtained by the partial evaporation of solvent was recrystallised twice from petroleum ether (40-60°) melting at 80°C. $C_{12}H_8N_2O_2$ requires % C = 67.92, H = 3.72, N=13.2; found % C = 67.81, H = 3.71, N = 13.07. I. R. spectrum in KBr shows bands at 3120, 3050 cm^{-1} for ν C-H, at 1595, 1535, 1490, 1370 cm^{-1} for ν ring, and at 930, 890, 865, 840, 775 cm^{-1} for γ C-H vibrations. Mass spectrum shows a peak at m/e 212 (100%) corresponding to molecular ion. The other main peaks are at m/e 183 (22.7%), 155(19%), 118(2.7%), 93(53.6%), 65(13.6%).

Solutions

Solutions of iron(II), iron(III), copper(II), cobalt (II) and nickel(II) were prepared containing 1mg/ml from pure $FeSO_4 . 7H_2O$, pure $NH_4 Fe(SO_4)_2 . 12H_2O$, pure $CuCl_2 . 2H_2O$ pure $CoCl_2 . 6H_2O$, and $NiCl_2 . 6H_2O$ respectively. A range of conventional buffer solutions was prepared containing where appropriate one or more of the following:

Hydrochloric acid, acetic acid (2M), sodium acetate (2M), ammonium acetate (2M), ammonium chloride (2M) and aqueous ammonia.

Solutions at unit pH intervals in the range of 1-10 were thus obtained.

Solution (0.2%) of organic reagents were prepared before use by dissolving required amount in ethanol. A freshly prepapred 1% aqueous solution of ascorbic acid was used for reduction of copper(II) and any iron(III) present in iron(II) solutions.

Qualitative Studies.

Qualitative studies of complex formation with Fe(II), Cu(I), Ni(II), Co(II) was carried out as under:

To each of several semi-micro test tubes were added in turn one drop of metal solution, 2 drops of 1% ascorbic acid, 5 drops of particular organic reagent and 10 drops of buffer solution (different in each tube and covering the range pH 1-10). The formation of any colour and its variation with pH were noted. The solutions were allowed at room temperature and any change in colour or precipitate formation with time was also noted. Chloroform and 1,2-dichloroethane were used to assess the extractability of the complexes. Qualitative studies of complex formation with iron(III) and copper(II) were carried out using same procedure except use of ascorbic acid was omitted.

Spectrophotometric Studies.

Spectrophotometric studies of the reactions of the reagents towards iron(II), copper(I), cobalt(II) and nickel(II) was carried out as under:

Exactly 0.5 ml of the metal ion solution was transferred to 25 ml volumetric flasks and 1 ml of 1% freshly prepared ascorbic acid solution and 5ml of organic reagent solution was added, followed by 5 ml of particular buffer solution. The contents were diluted to volume with water or ethanol and solutions were allowed to remain at room temperature (0.25 to 3 hours) for colour development. The absorption specturm of the solution in the visible region was recorded with Beckmann BD Prism spectrophotometer against reagent blank in appropriate solvent before the solution became turbid.

Similarly absorptiometric studies of Fe(III) and Cu(II), was carried out following same procudure except the addition of ascorbic acid was omitted.

All pH measurements were carried out using WTW DIGI Model 88 pH meter with combined glass electrode.

All I.R. spectra were recorded using KBr and nujol mull techniques with Unicam SP 1025 I.R. spectrophotometer.

Elemental micro-analysis of the organic materials were determined by Elemental Micro-Analysis Ltd., U.K.

Mass-spectra of the compounds were recorded by HEJ Research Institute of Chemistry, University of Karachi.

Results and Discussion

The reagents reported in the present work do not contain characteristic -N=C-C = N- ferroin reactive atomic grouping, but the atomic sequence -O-C-C = N-C-C = N-C-C-O- and-N = C-C-O-, containing O and N atoms suitably placed for complexation are present in bis (furfural) ethylenediimine, and 2,3-bis(2furyl)-5,6-dihydropyrazine and 2,3-bis(2-furyl) pyrazine respectively.

The results of qualitative and spectrophotometric studies are summarized in table 1, in which the properties of metal complexes of the reagents are compared. The results indicate that the reagents react in similar fashion to form coloured complexes slowly between pH 4-6. The complexes eventually precipitate out or form turbid solution in aqueous-ethanolic solution, except the copper(II) complex of bis (furfural) ethylenediimine which develops blue colour immediately without formation of precipitate or turbiditing in 24 hours.

Bis(furfural)ethylenediimine. The reagent prepared by simple condensation of two moles of furfural and one mole of ethylenediamine showed diagonastic bands in its I.R. spectrum at 3120 and 3080 cm^{-1} for aromatic=C-H stretching vibrations of furyl rings and at 1645 cm^{-1} for C=N vibrations. Mass spectrum indicated molecular ion peak at m/e 216 and base peak at m/e 108, at half of the molecular ion peak due to the breakage of-CH_2-CH_2- group. The remaining peaks also follow standard fragment pattern expected from its structure.

The result of qualitative studies indicated that excess of the reagent when added to the metal ion solution of Fe(II), Fe(III), Cu(I),Co(II), Ni(II) developed yellow colour, but iron(II) changed to brown colour which produced turbidity quickly in ethanolic solution. However in mixture of ethanol: water the absorbance of the solution was measured before it became turbid. On the other hand copper(II) developed immediately blue colour which did not change in absorbance in 24 hours. The metal ions Fe(III), Cu(II), Co(II) and Ni(II) metal ions developed colour slowly which formed yellow to orange turbidity or precipitate within 24 hours.

2,3-Bis(2furyl)-5,6-dihydropyrazine. The reagent prepared by simple condensation of furil and 1,2-diminoethane indicated the bands at 3140 and 2950 cm^{-1} in its I.R. spectrum corresponding to the C-H stretching vibrations of furyl and dihydropyrazine rings respectively. Mass spectrum indicated that the dihydropyrazine ring opened and molecule split in two portions showing a peak at m/e 93(100%) (C_5H_3NO) and other at m/e 121. The latter peak again lost successively mass units corresponding to two -CH_2 groups to produce same base peak ion at m/e 93.

The results of the qualitative studies of the reactions towards metal ions indicated that the mixing of the reagent to the metal ion solution between pH 1-10 in aqueous ethanolic solution did not develop any colour immediately, however iron(II) solution between pH 4-6 changed to brown rapidly particularly in ethanolic solution. Similarly copper(I), nickel (II), and cobalt(II) developed yellow to orange colour which precipitated out within 24 hours between pH 4-6.

It is striking to note that the reagent indicated colour reaction with Fe(II), Cu(I), Ni(II) and Co(II), and it failed to produce any colour reaction with Fe(III) and Cu(II), similar to typical ferroin type reactions.

2,3-Bis(2-furyl) pryazine. The I.R. spectrum of the reagent in KBr showed the bands at 3120 and 3050 cm^{-1} for aromatic C-H stretching vibrations of furyl and pyrazine rings. Mass spectrum produced the molecular ion peak as base peak characteristic of aromatic compounds. The fragment pattern indicated the opening of furyl rings with à strong peak at a m/e 93(53%.6%) corresponding to the formula $C_5H_5N_2$ containing pyrazine ring.

The results of qualitative studies also indicated similar behaviour to form coloured complexes slowly with Fe(II), Cu(I), Ni(II) and Co(II) between pH 4-6. The brown colour of iron(II) complex showed a broad band spreading in whole of the visible region with λmax at 520 nm and 492 nm. Copper(I), nickel (II) and cobalt (II) reacted similarly with the reagent to form yellow to orange colour which precipitated

Table 1. Qualitative Studies and Absorptiometric Data of the Reagents and their Metal complexes.

Reagent	Metal ion	Solvent	pH of the measurements	λ-max nm	ε. 1. $mole^{-1}$ cm^{-1}	Absorbance measured after the preparation of solution	Colour	Reaction after 24 hours
Bis(furfural) ethylenediimine	–	Ethanol	–	310 220	5400 52650	–	–	–
	Fe(II)	Ethanol: water (I:1)	4.6	450	7231	1 hr	yellow changed to brown	brown ppt.
	Fe(III)	Ethanol: water: (1:1)	4.6	418	307	3 hrs	yellow	yellow turbid solution.
	Cu(I)	Ethanol	6	385 378	1013	1.5 hr	yellow	turbid orange
	Cu(II)	Ethanol	6	650	64	immediate	blue colour	blue colour
	Co(II)	Ethanol	6	410	2654	1.5 hr	orange	orange turbidity
		Ethanol: water (I:I)	6	404	2948	1.5 hr	yellow	orange turbidity
	Ni (II)	Ethanol	6	397	1758	1.5 hr	yellow	yellow turbid solution
		Ethanol: Water (1:1)	6	387	1347	1.3 hr	yellow	yellow turbid
2,3-bis(2-furyl)-5,6-dihydropyrazine	–	Ethanol	–	309 288 234	8132 10700 10700	–	–	–
	Fe(II)	Ethanol: water (I:I)	4.6	500 400	838 1329	2 hrs	brown	brown ppt
	Cu(I)	Ethanol	6	390	794	1 hr	yellow	yellow
		Ethanol: Water (1:1)	6	392	1267	1.5 hr	yellow	yellow ppt
	Co(II)	Ethanol	6	402	1253	2 hrs	yellow	orange ppt

Table 1 (Continued)

		Ethanol: Water (1:1)	6	398	2830	2 hrs	yellow	orange ppt
	Ni(II)	Ethanol	6	406	2197	0.5 hr	yellow	orange ppt
		Ethanol: Water(1:1)	6	406	2197	0.5 hr	yellow	dark orange ppt.
2,3-bis(2-furyl)pyrazine	–	Ethanol	–	305 278 220	10070 14840 12720	–	–	–
	Fe(II)	Ethanol: Water (1:1)	4.6	520 492	1145 2345	1.25 hr	brown	brown ppt
	Cu(I)	Ethanol	6	394	2915	2.5 hr	yellow	orange ppt
		Ethanol: Water (1:1)	6	387	1140	2 hr	yellow	orange ppt
	Cu(II)	Ethanol: Water (1:1)	6	390	3010	15 hrs	yellow	orange ppt
	Co(II)	Ethanol	6	405	5012	1 hr	yellow	orange ppt
	Ni(II)	Ethanol	6	400	4981	1 hr	yellow	dark orange ppt
	Ni(II)	Ethanol: Water (1:1)	6	400	3516	1 hr	yellow	orange ppt

out within 24 hours. Copper(II) did not indicate complex formation, however it developed some yellow colour after standing at room temperature ($30^{o}C$) for 15 hours which eventually changed in turbid solution in 24 hours.

Conclusion.

The reagents have been prepared by simple synthetic routes but suffers from the disadvantage that the rate of complex formation is slow and the metal complexes are not sufficiently sensitive spectrophotometerically. It is suggested that the complexation involves both nitrogen and oxygen atoms to from bis and tris complexes, but the complexes failed to extract in chloroform and 1,2-dichloroethane indicating that the complexes are highly solvated. The blue colour of copper(II)- complex of bis(furfural) ethylenediimine which failed to form precipitate or turbidity probably involves only both nitrogen atoms to form blue colour similar to ethylenediamine, but exact nature of the complexes has to be determined.

The reagents are easy to prepare and provides a good example for the group action among the molecules towards their reactions with metal ions.

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