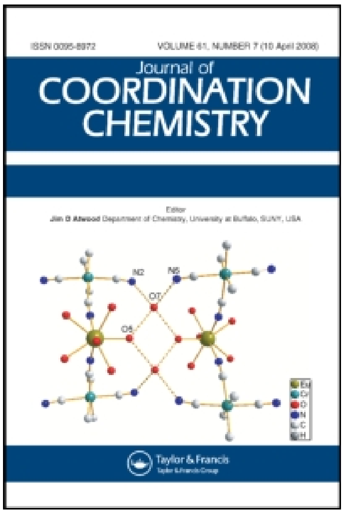

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COMPLEXES OF Cu(II), Co(II) AND Ni(II) WITH 2,3-BIS(2-PYRIDYL)PYRAZINE 1,4-DIOXIDE AND 2,3-BIS(2-PYRIDINE N-OXIDE)PYRAZINE

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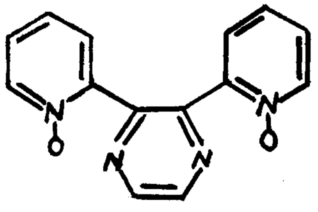
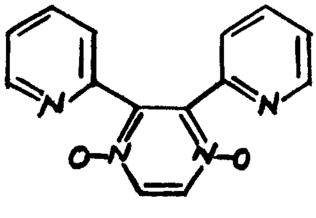
Two new ligands, *viz.* 2,3-bis(2-pyridyl)pyrazine 1,4-dioxide and 2,3-bis(2-pyridine N-oxide)pyrazine, and their complexes with cobalt(II), nickel(II) and copper(II) have been prepared. A detailed investigation of the magnetic and spectral properties of these compounds has led to some tentative suggestions as to their structures. All the complexes of 2,3-bis(2-pyridyl)pyrazine 1,4-dioxide and polymeric octahedral in structure and of the general formula $[MX_2L]_n$, but the complexes of 2,3-bis(2-pyridine N-oxide) follow a less ordered pattern.

INTRODUCTION

In our earlier paper, we reported the complexes of 2,3-bis(2-pyridine N-oxide)quinoxaline. (1) As an extension of this work, two similar ligands, namely, 2,3-bis(2-pyridine N-oxide) pyrazine (I) and 2,3-bis(2-pyridyl)pyrazine 1,4-dioxide (II) were prepared by direct oxidation, under different conditions, of 2,3-bis(2-pyridyl)pyrazine. The Co(II), Ni(II) and Cu(II) complexes of these two new ligands have been studied.



(I)



(II)

EXPERIMENTAL

Starting Materials

Commercially available analytical grade metal salts were used without further purification.

2,3-bis(2-pyridyl)pyrazine was prepared and purified using the method of Goodwin and Lions (2).

Preparation of Ligands

2,3-Bis(2-pyridine N-oxide)pyrazine (I) (hereafter called PPyNO). 10 gm of 2,3-bis(2-pyridyl)pyrazine were dissolved in 50 ml of 40% peracetic acid, and the solution was heated at 50°C for 20 hours. The reaction mixture was then diluted to 200 ml with water and neutralized with 40% NaOH solution (an excess of base would decompose the product). The yellow precipitate formed was separated out by filtration and washed several times with distilled water. It was recrystallized from glacial acetic acid, m.p. = 325°C (decomposed). Anal. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.16; N, 21.05; O, 12.03; H, 3.76. Found: C, 63.07; N, 21.34; O, 12.05; H, 3.35.

2,3-Bis(2-pyridyl)pyrazine 1,4-dioxide (II) (hereafter called PNOPy) 5 gm of 2,3-bis(2-pyridyl)pyrazine were dissolved in 30 ml conc. H_2SO_4. This acid solution was added dropwise with stirring into a mixture of 100 ml conc. H_2SO_4 and 50 ml 30% H_2O_2, while maintaining the temperature of the mixture between 10–20°C for one hour. Then, the reaction mixture was allowed to stand at room temperature for two days. At the end of this period, the mixture was poured onto cracked ice, neutralized with NaOH solution and extracted with chloroform. The extract, after the removal of the chloroform by evaporation, yielded a yellow product which was subsequently recrystallized from ethanol, m.p. = 234–235°C. Anal. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.16; N, 21.05; O, 12.03; H, 3.76. Found: C, 63.11; N, 21.08; O, 12.23; H, 3.65.

Preparation of Complexes

All the complexes of PNOPy were prepared similarly as before (1).

Complexes of PPyNO were prepared by the Soxhlet extraction method, since the ligand is only slightly soluble in ethanol. An excess of the metal salts in ethanol was introduced into the round bottom flask. PPyNO wrapped in a piece of filter paper, was put inside an extraction thimble which was placed into the extraction Soxhlet. The extraction was continued for 24 hours. The complexes were precipitated either during the extraction or upon the removal of a quantity of solvent. After purifying by thorough washing with ethanol, the complexes were dried in a desiccator.

Analytical data for all of the complexes are given in Table I and II.

Magnetic and Spectrophotometric Measurements

Magnetic and spectrophotometric measurements were obtained as described previously (1).

All the magnetic and electronic spectral data are listed in Tables III and IV.

The nuclear magnetic resonance spectra were obtained on a Varian Associates Model T-60 spectrometer using tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

(I) The Structure of the Ligands

Direct oxidations of 2,3-bis(2-pyridyl)pyrazine (which has four nitrogen atoms available for oxidation) under different conditions, give two isomers, *viz.* PPyNO and PNOPy. The physical properties of these two isomers are quite different. PNOPy has a lower melting point and is soluble in most organic solvents; PPyNO has a higher melting point (decomposed) and is only sparingly soluble in ordinary

TABLE I
Analytical data of complexes of PNOPy

		Found %				Calculated %			
Complexes	Color	M	X	C	H	M	X	C	H
$CuCl_2(PNOPy)\cdot 2H_2O$	Green	14.64	16.60	38.42	3.22	14.56	16.26	38.48	3.21
$CuBr_2(PNOPy)\cdot 2H_2O$	Green	12.34	30.59	32.43	2.71	12.10	30.42	21.99	2.67
$NiCl_2(PNOPy)\cdot 3H_2O$	Red-Brown	13.44	15.85	37.56	3.80	13.06	15.79	37.36	3.56
$NiBr_2(PNOPy)\cdot \frac{1}{2}H_2O$	Brown	12.17	32.64	34.14	2.32	11.89	32.38	34.04	2.23
$NiI_2(PNOPy)\cdot 2H_2O$	Brown	9.63	41.05	27.19	2.18	9.55	41.30	27.34	2.28
$CoCl_2(PNOPy)\cdot \frac{1}{2}H_2O$	Red-Brown	14.67	17.58	41.83	2.77	14.55	17.54	41.47	2.72
$CoBr_2(PNOPy)\cdot \frac{1}{2}H_2O$	Brown	12.23	32.68	34.39	2.38	11.94	32.37	34.03	2.23
$CoI_2(PNOPy)\cdot H_2O$ [a]	Brown	10.24	42.50	28.32	2.09	9.87	42.54	28.16	2.01

[a] Prepared under N_2. X = halogen

TABLE II
Analytical data of complexes of PPyNO

Complexes	Color	Found % M	Found % X	Found % C	Found % H	Calculated % M	Calculated % X	Calculated % C	Calculated % H
$CuCl_2(PPyNO)\cdot H_2O$	Green-brown	15.20	16.96	40.32	3.01	15.17	16.97	40.14	2.87
$NiCl_2(PPyNO)_2\cdot 7H_2O$	Yellow	7.72	9.14	42.87	4.11	7.45	9.01	42.66	4.32
$NiBr_2(PPyNO)_2\cdot 8H_2O$	Yellow	6.81	17.79	37.91	4.31	6.56	17.87	37.56	4.03
$NiI_2(PPyNO)_2$	Red-brown	7.08	30.31	39.58	2.30	6.95	30.05	39.79	2.37
$CoCl_2(PPyNO)\cdot 4H_2O$	Green	12.34	15.56	36.08	3.98	12.59	15.17	35.90	3.85
$CoBr_2(PPyNO)\cdot H_2O$	Green	12.00	31.77	33.31	2.17	11.72	31.79	33.42	2.39

TABLE III
Room temperature – magnetic moments and electronic spectra of complexes of PNOPy

Complexes	μ (B.M.)	Electronic Spectra (nm)[a]
$CuCl_2(PNOPy)\cdot 2H_2O$	1.89	390(sh); 770
$CuBr_2(PNOPy)\cdot 2H_2O$	1.81	400(sh); 800
$NiCl_2(PNOPy)\cdot 3H_2O$	3.16	380(sh); 534; 1170(w); 1470(vw)
$NiBr_2(PNOPy)\cdot \frac{1}{2}H_2O$	3.10	390(sh); 530; 1143(w); 1401(vw)
$NiI_2((PNOPy)\cdot 2H_2O$	3.08	400(sh); 586; 1050(w); 1200(w)
$CoCl_2(PNOPy)\cdot \frac{1}{2}H_2O$	4.81	520; 590(sh); 1080(w); 1200(vw)
$CoBr_2(PNOPy)\cdot \frac{1}{2}H_2O$	4.85	520; 620(sh); 1200(w)
$CoI_2(PNOPy)\cdot H_2O$	483	400(sh); 600(sh); 1220(w); 1470(w)

[a] sh = shoulder, w = weak, vw = very weak.

TABLE IV
Room temperature – magnetic moments and electronic spectra of complexes of PPyNO

Complexes	μ (B.M.)	Electronic Spectra (nm)[a]
$CuCl_2(PPyNO)\cdot H_2O$	1.84	392; 764
$NiCl_2(PPyNO)_2\cdot 7H_2O$	3.31	368; 550(w); 1060(w); 1210(w)
$NiBr_2(PPyNO)_2\cdot 8H_2O$	3.34	374; 560(w); 1070(w); 1190(w)
$NiI_2(PPyNO)_2$	3.15	390(sh); 580(w); 1100
$CoCl_2(PPyNO)\cdot 4H_2O$	4.79	366; 640; 676; 1500(w)
$CoBr_2(PPyNO)\cdot H_2O$	4.31	370; 646; 696; 1560(w)

[a] w = weak.

solvents. Both analytical and mass spectral data for the two compounds indicate that even under different oxidation conditions, only two of the four nitrogen atoms are accessible to oxidation. The infrared spectra of PPyNO and PNOPy show the presence of N–O stretching bands at 1251 and 1216 cm^{-1}, and at 1243 and 1233 cm^{-1} respectively. However, from these experimental results, no definite information on the exact locations of the two oxygen atoms can be drawn. The NMR spectra of PNOPy in deuterated chloroform and PPyNO in trifluoroacetic acid show a single proton magnetic resonance absorption band at 8.20 τ and 10.17 τ respectively. By comparing with the NMR spectrum of 2,3-bis(2-pyridyl)pyrazine, these bands can be assigned as the absorption of the two protons on the pyrazine ring, and their singlet nature indicates that these two protons are chemically equivalent. This suggests that the two oxygen atoms are bonded symmetrically either to the pyridine rings or the pyrazine ring. The NMR spectrum of PNOPy, when compared with that of 2,3-bis(2-pyridyl)pyrazine, shows a large shift in the absorption band of the two pyrazine protons, while the other absorption bands of the pyridine protons remain almost unchanged indicating that in PNOPy, the oxygen atoms are bonded to the pyrazine ring. Similar analysis of the NMR spectrum of PPyNO indicates that besides the shift of the single absorption band of the two pyrazine protons, the absorption bands of the pyridine protons are also shifted. This confirms that in PPyNO, the oxygen atoms are bonded to the nitrogen atoms of the pyridine rings.

Molecular models were constructed for PNOPy and PPyNO, and showed that the most probable geometry for these ligands to form metal chelates was to place the two pyridine rings or pyridine N-oxide rings parallel and approximately 45° to the plane of pyrazine 1,4-dioxide or pyrazine respectively.

(II) The Structure of Metal Complexes

The two new ligands, PNOPy and PPyNO, both containing coordinating oxygen and nitrogen atoms, can act either as mono-bidentate and/or bis-bidentate chelating agents. When they are acting as mono-bidentate chelating agents, the steric effect associated with them is very similar. However, when they are acting as bis-bidentate chelating agents, an important structural difference between PPyNO and PNOPy occurs in their complexes. In complexes where PNOPy is acting as a bis-bidentate chelating agent, the metal ions are situated in a trans position, i.e., one metal ion is above, and the other below the plane of the pyrazine 1,4-dioxide ring (III). However, in complexes of PPyNO, the metal ions reside on the same side of the pyrazine ring (IV). In this latter arrangement, the distance between the two metal ions is shorter than that of the PNOPy complexes where the metal ions are in a trans position.

Cobalt Complexes

Both cobalt(II) chloride and bromide complexes of PPyNO are tetrahedral in structure, with the ligand acting as mono-bidentate agents. Their magnetic moments are 4.79 and 4.31 B.M. respectively (3). Their electronic spectra show multiple absorption bands at 600–700 nm and 1500–1600 nm, and are assigned as the $^4T_1(P) \leftarrow {}^4A_2$ and $^4T_1(F) \leftarrow {}^4A_2$ transitions respectively (4).

Several efforts have been attempted to prepare the cobalt(II) iodide complex of PPyNO. However, the brown precipitate obtained was impure and could not be further purified.

On the other hand, cobalt(II) halides formed polymeric octahedral complexes with PNOPy. Their electronic spectra showed absorptions in the region 500–620 nm and 1100–1250 nm, which are characteristic of octahedral cobalt complexes (4). The magnetic moments of 4.81–4.85 B.M. for all three complexes also indicate their octahedral structures, though the moments at the lower end of the octahedral range are usually taken to indicate strong tetragonal distortions (5). The polymeric geometry requires PNOPy to be a bis-bidentate bridging ligand.

Nickel Complexes

The characteristics of the electronic absorption bands of all the nickel complexes indicate that they have octahedral structures, in agreement with the magnetic moments of 3.08–3.34 B.M. for these complexes. Three absorption bands in the region of 370–400 nm, 530–600 and 1050–1400 nm are assigned as the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{2g} \leftarrow {}^3A_{2g}$ transitions respectively. In most cases, the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition band appears as a shoulder due to the tailing of the strong ligand absorption band near 320 nm.

For the complexes of $NiCl_2(PPyNO)_2 \cdot 7H_2O$, $NiBr_2(PPyNO)_2 \cdot 8H_2O$ and $NiI_2(PPyNO)_2$, it is obvious that an octahedral structure is formed when each of the two PPyNO ligands acts as a mono-bidentate agent. The water molecules are not coordinated to the metal ion and can be removed by heating to 100°C.

For the nickel halide complexes of PNOPy, in addition to the electronic spectra and magnetic data suggesting octahedral structures, their infrared spectra are essentially the same as that of the corresponding cobalt complexes. Therefore, a similar polymeric octahedral structure is assigned to the nickel complexes of PNOPy.

Copper Complexes

All the copper complexes showed a single broad band around 700–800 nm, and are characteristic of six-coordinated copper. Thus, a tetragonal environment commonly found for the Cu(II) ion is expected in these complexes with PPyNO and PNOPy coordinating as bridging bis-bidentate ligands.

Reactions of copper halides with PPyNO or PNOPy in alcoholic solutions lead to the immediate formation of complexes of the formula $CuLX_2$. However, when the $CuBr_2$ complex of PPyNO was prepared, a large amount of black precipitate formed at the beginning, and was later identified as copper oxide. After the removal of this black precipitate by filtration, a green compound gradually formed from the filtrate. The electronic spectrum of this green complex shows an absorption at 782 nm and its infrared spectrum is similar to that of the $CuCl_2(PPyNO)$ complex, indicating that it also has a polymeric octahedral structure. However, the analytical results of this green compound do not agree with the values for $CuBr_2(PPyNO)$. It is assumed that a small amount of copper oxide co-precipitates with the green complex.

CONCLUSION

The ligand PPyNO forms a wide range of complexes of different stoichiometry and structure with Co(II), Ni(II) and Cu(II) ions. It seems to be very difficult to predict the general behaviour of PPyNO. On the other hand, all the complexes of PNOPy are polymeric octahedral in structure. As has been discussed earlier, when PNOPy is acting as a bis-bidentate chelating agent, the metal ions will be situated trans to each other. This particular arrangement of the metal ions has the effect of increasing the distance between them, decreasing their steric hindrance, and as a result, rendering the ligand to be more favorable to act as a bis-bidentate bridging agent.

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