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Studies on Manganese(II), Iron(II), Cobalt(II), Nickel(II) & Copper(II) Complexes with Pyrazine Amides

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Some transition metal complexes of pyrazine-2-amide and pyrazine-2, 3-diamide have been prepared and characterized. Three types of complexes have been isolated: (a) non-deprotonated amide complexes with N (hetero), O (amide) coordination; (b) deprotonated amide complexes of Cu(II) and Ni(II) with N(hetero), N(amide) coordination; and (c) a deprotonated N(hetero), O(carboxyl) complex of Cu(II) with pyrazine-3-amide-2-carboxylic acid, presumably obtained from hydrolysis of pyrazine-2, 3-diamide ligand.

Heterocyclic carboxamides having pyridine or pyrazine moiety are known to possess antitubercular activity[1]. In view of their biological and therapeutic significance, studies on several transition metal complexes with pyrazine-2-amide[2,3] picolinamide[4], nicotinamide[2] and to a lesser extent with pyrazine-2, 3-diamide[2,5-7] have been made. The present paper describes the isolation and characterisation of some complexes of transition metal ions with pyrazine-2-amide and pyrazine-2, 3-diamide. Three types of complexes have been isolated: complexes with non-deprotonated amide ligand (type-a); complexes with deprotonated amide group (type-b); and complex with deprotonated carboxyl group generated by the hydrolysis of an amide group (type-c).

Materials and Methods

The metal salts used were either of AR (BDH) or GR(EM) quality except the bromides that were prepared in our laboratory. Pyrazine-2-amide and pyrazine-2, 3-diamide were obtained from EGA-CHEMIE, West Germany and used without further purification.

Preparation of metal complexes: complexes of type (a)—The Mn(II) complex with pyrazine-2-amide was prepared by refluxing a mixture of solutions of the ligand and $MnCl_2.4H_2O$ (3:1) in *t*-butyl alcohol and cooling the mixture to room temperature when a light-yellow compound separated; it was washed with hot solvent and dried *in vacuo* over $CaCl_2$.

The Fe(II) perchlorate complex with pyrazine-2-amide was prepared and worked up similarly as above except that solid metal salt was added to the ligand solution (1:2) before refluxing. The Fe(II) chloride complex was prepared similarly using ethanol as solvent in place of *t*-butyl alcohol.

Owing to very poor solubility of pyrazine-2, 3-diamide in common organic solvents, an indirect method was developed for the preparation of its complexes with Co(II), Ni(II) and Cu(II). The ligand got dissolved completely upon refluxing its suspension in dry methanol in presence of excess cobalt/nickel salts presumably due to complex formation. From resulting clear solution [solution (A)] thus obtained the cobalt/nickel complexes were isolated after concentrating and cooling. The crystals were washed with methanol [except for the nitrate and chloride complexes of Co(II) which were filter-pressed to avoid decomposition during washing; crystals were sufficiently pure for further study] and dried as above.

The Cu(II) complexes were prepared by adding corresponding copper salts to solution (A) as prepared above and refluxing; the crystals which slowly separated were filtered, washed and dried as above.

Complexes of type (b): nickel(II) *complex with deprotonated pyrazine-2-amide,* $[Ni(PzA\text{-}H)_2]$—To about 0.2 g of $Ni(NO_3)_2.6H_2O$ dissolved in about 2 ml of formamide was added dropwise strong NH_4OH until a bluish-violet colour appeared (*p*H ~ 9). To the solution was then added solid pyrazine-2-amide (~ 0.35 g) and the suspension was slightly warmed on a water-bath when a compound appeared on swirling. The compound was filtered, again refluxed with dry ethanol to remove excess of ligand and metal salt, filtered, washed with dry ethanol and dried in air.

Copper(II) complex with deprotonated pyrazine-2, 3-diamide-$[Cu(Pzda\text{-}H)_2]$ 0.2 g of $[Cu(NH_3)_4]SO_4.H_2O$ was dissolved in a small amount of water containing 1-2 drops of strong NH_4OH and added to an aqueous solution of 0.25 g of the ligand (10 ml) and the mixed solution was kept at room temperature when the precipitate appeared slowly; it was filtered, washed with water containing a little NH_4OH and finally dried *in vacuo* over CaO.

Copper(II) complex with partially hydrolysed pyrazine diamide, $[Cu(pz\text{-}3\ CONH_2.2COO)_2.4H_2O]$

(*type c*)—The complex was obtained in the form of shining green crystals when an aqueous solution, containing a few drops of dil. HCl, of a mixture of copper chloride and pyrazine-2, 3-diamide (1:2) was kept on a steam-bath for 4-5 hr, concentrated and kept at room temperature. The crystals obtained were filtered, washed with water and dried in air.

The metals were analysed gravimetrically after decomposing the complexes with conc. nitric and sulphuric acids [copper and cobalt using 2-quinoxaline carboxylic acid[8], nickel with dimethylglyoxime, iron gravimetrically as oxide]. Manganese was estimated titrimetrically after conversion into MnO_4^-. Nitrogen content (amide) was analysed by heating the sample with strong alkali and absorbing ammonia liberated in excess of standard sulphuric acid and titrating back the excess acid against a standard alkali. Nitrate was analysed[9] after distilling away all ammonia from amide, adding Devarda's alloy to the cooled kjeldahl flask and again distilling and estimating ammonia as mentioned above. The chlorine content was estimated as silver chloride after fusion of the complexes with sodium peroxide and treatment as usual. Bromine content was estimated after decomposing the sample according to procedure given by Wurtzschmidt[10], extracting the mass with water, boiling to decompose excess of sodium peroxide, acidifying and boiling again with sulphurous acid solution to reduce any bromate produced and precipitating and weighing as silver bromide. Carbon and hydrogen were analysed at the Alfred Bernhardt Laboratories, West Germany. The results of analyses are shown in Table 1.

The magnetic moments were measured with a Gouy balance using Hg [$Co(SCN)_4$] as the calibrant, and diamagnetic corrections were applied[11]. Spectra in the solid state were recorded in nujol on a spectromom-204 (Hungary) instrument. Reflectance spectra were recorded on a Cary 17 spectrophotometer at IACS, Calcutta. Conductance as well as spectra in the solution form of the complexes could not be recorded owing to their poor solubilities in non-aqueous solvents; in aqueous medium the complexes decomposed. Infrared spectra in the region 400-

Table 1—Elemental Analyses, Colour and Magnetic Moments of Metal Complexes of Pyrazine-2-amide (PzA) and Pyrazine-2, 3-Diamide (Pzda)

Complex	Colour	μ_{eff} (B.M.) at 27 C	Found (Calc), %		
			M	N(amide)	Anion
$Mn(PzA)_2Cl_2$	Light-yellow	5.97	14.80 (15.00)	7.68 (7.52)	18.74 (19.11)
$Fe(PzA)_2Cl_2$	Red	5.42	15.25 (14.97)	7.60 (7.50)	18.82 (19.06)
$Fe(PzA)_2(ClO_4)_2$	Red	5.30	11.05 (11.15)	5.60 (5.59)	— —
$Ni(PzA\text{-}H)_2$	Red	Diamagnetic	19.56 (19.50)	9.37 (9.25)	—
$Cu(Pzda)Cl_2$	Green	1.93	21.00 (21.13)	9.50 (9.32)	22.80 (23.63)
$Cu(Pzda)_2Br_2.2H_2O$	Light-green	1.84	10.96 (10.74)	9.66 (9.45)	27.15 (27.05)
$Cu(Pzda)_2(NO_3)_2H_2O$	Blue	1.96	11.93 (11.81)	10.05 (10.42)	22.86 (23.07)
$Cu(Pzda\text{-}H)_2$	Brown	1.93	15.96 (16.06)	13.65 (14.16)	
$Ni(Pzda)_2Cl_2$	Yellow	3.03	13.36 (12.72)	11.64 (12.13)	15.29 (15.42)
$Ni(Pzda)_2Br_2$	Yellow	3.09	11.24 (10.66)	9.75 (10.17)	30.15 (29.05)
$Ni(Pzda)_2(NO_3)_2.2H_2O$	Light-green	3.14	11.00 (10.66)	10.34 (10.17)	24.60 (22.52)
$Co(Pzda)_2Cl_2$	Chocolate	5.19	11.90 (12.76)	11.84 (11.85)	16.20 (15.38)
$Co(Pzda)_2Br_2$	Yellow	4.76	11.03 (10.69)	9.79 (10.16)	28.36 (29.04)
$Co(Pzda)_2(NO_3)_2.2H_2O$	Yellow	4.84	12.50 (10.69)	10.50 (10.16)	22.12 (22.51)
$Cu(Pz\text{-}3\text{-}CONH_2\text{-}2\text{-}COO)_2.4H_2O$	Green	1.70	13.48 (13.59)	6.22 (5.98)	—

4000 cm $^{-1}$/650-4000 cm $^{-1}$ were recorded in KBr at the CDRI, Lucknow, and in the region 200-650 cm $^{-1}$ in nujol mulls between polystyrene sheets at the Department of Chemistry, University of West Indies.

ESR spectra of some copper(II) compounds were recorded in the powder form at liquid N_2 temperature at the RSIC, Madras.

Results and Discussion

The IR spectra of pyrazine-2-amide complexes of $FeCl_2$ and $MnCl_2$ are almost identical indicating thereby similar ligand environment around both the metals. In both these complexes the symmetric and antisymmetric OCN stretches are little affected compared to their positions in the ligand (1710-1720 and 1374 cm $^{-1}$ respectively) implying participation of amide group in bonding. In both complexes the pyrazine ring out-of-plane deformation band is shifted to higher frequency (460 and 450 cm $^{-1}$ respectively) relative to the free ligand (435 cm $^{-1}$) indicating coordination of ring nitrogen to the metals. Again presence of medium intensity bands at 955 and 950 cm $^{-1}$ shows the existence of terminal pyrazine in the complexes[12]. Moreover, bands occurring at 230(w) and 248(m; br)) cm $^{-1}$ for $FeCl_2$ and at 235(s) cm $^{-1}$ for $MnCl_2$ may be due to M-X stretches that are probably bridging[13,14]. The pyrazine-2-amide complex of $Fe(ClO_4)_2$, however, shows large positive and negative shifts (~ 35 cm $^{-1}$) in the symmetric and antisymmetric νOCN modes respectively indicating thereby that the oxygen atom of the amide group is involved in coordination to the metal. There is a weak splitting of ClO_4 bands around 1100 cm $^{-1}$ which is indicative of its ionic nature.

In the Ni(II) complex of deprotonated pyrazine-2-amide the ν_{as}OCN is shifted to a more negative value and the ν_sOCN remains almost unshifted. This indicates that the amide nitrogen coordinates to the metal[3]. Again presence of a medium sharp band at 1288 cm $^{-1}$ (which is absent in the free ligand) indicates coordination by deprotonated amide nitrogen[15]. Moreover, the general reduction in intensity of the NH_2 vibrational modes is in conformity with the presence of singly deprotonated species.

Pyrazine-2, 3-diamide shows ν_{as}OCN at 1680 and 1695 cm $^{-1}$ and ν_sOCN at 1348 and 1395 cm $^{-1}$. The Cu(II) complex of deprotonated pyrazine-2, 3-diamide (type-b) shows the ν_{as}OCN at 1650 cm $^{-1}$ while the ν_sOCN remain almost unshifted suggesting that coordination occurs through nitrogen atom of the deprotonated amide group. Moreover, presence of two bands at 1285 (ms) and 1270 (sh) cm $^{-1}$ in the complex further suggests bonding through N-atom of the deprotonated amide group (such bands are absent in the free amide ligand as well as in ionic complexes) since bending vibrations of coordinated NH groups in N-bonded complexes are found to occur in the region[15].

In the complexes of non-deprotonated diamide, negative and positive shifts respectively in the ν_{as}OCN and ν_sOCN occur indicating coordination through oxygen atom of the amide group[3]. The $CoCl_2$ complex shows negligible shifts and therefore the amide groups remain uncoordinated, similar to the behaviour in the complex with pyrazine-2-amide[16]. In all the complexes, except that with $CuCl_2$, presence of bands at ~1700 and ~1360 cm $^{-1}$ implies that one of the amide groups remains uncoordinated. The copper chloride complex has both $CONH_2$ groups coordinated since there are no bands at 1700 and at 1360 cm $^{-1}$ of the free amide group. Further, a strong band at 310 cm $^{-1}$, which can not be attributed to the ligand, is observed and it is probably due to terminal νCu-Cl[17].

In the metal nitrate complexes, the positions of the ν_sOCN band cannot be identified as it is obscured by strong nitrate absorptions. The spectra of the nitrate complexes are, however, very similar to those of the respective bromide complexes with regard to number of bands, band profile and band positions indicating similar bonding through oxygen atom of the amide group. The presence of a medium sharp band around 820-830 cm $^{-1}$ in addition to a very strong band around 1350 cm $^{-1}$ suggests that nitrates are ionic[18].

In all the complexes the pyrazine ring out-of-plane deformation at 428 cm $^{-1}$ is shifted to higher frequencies, a good indication of coordination of the heterocyclic nitrogen.

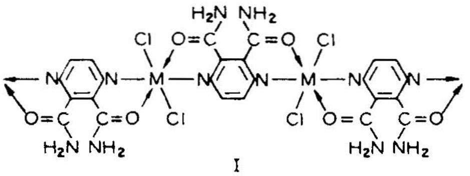
The copper complex (type-c) has a very broad νOH band around 3000-3500 cm $^{-1}$ which envelopes all NH_2 bands. However, it is difficult to ascertain whether water is coordinated or not since the typical bands of coordinated water are obscured by ligand bands. The compound shows bands at 1650 cm $^{-1}$ (s) and 1340 cm $^{-1}$ (s) corresponding to ν_{as}COO and ν_sCOO respectively. Again presence of bands at 1720 (sh) and 1382 (s) cm $^{-1}$ is indicative of a free $CONH_2$ group, the bands being very near to those of pyrazine-2-amide itself. Moreover, a strong band occurring at 1122 cm $^{-1}$ may be assigned to $\rho_r NH_2$ on comparison with the values of 1121 and 1105 cm $^{-1}$ for pyrazine-2-amide and pyrazine-2, 3-diamide respectively.

The magnetic moments observed for the metal complexes are shown in Table 1. The magnetic moments of the pyrazine-2-amide-iron(II) complexes are typical of high-spin Fe(II) ion in octahedral environment[19]. The high-spin complex of Mn(II) (d^5 system) is expected to show a magnetic moment very close to the spin-only value (5.92 B.M.). The Ni(II) complex with deprotonated pyrazine-2-amide is diamagnetic in agreement with its square-planar stereochemistry. The values observed for all the pyrazine diamide complexes of Cu(II), Co(II) and Ni(II) correspond to the reported ranges for the corresponding distorted octahedral structures[11,20].

The reflectance spectrum of the Mn(II) complex with pyrazine-2-amide shows bands at 340, 390 and 550 nm which are typical of octahedral arrangement. Although spin-forbidden electronic transitions are expected in both tetrahedral and octahedral fields, the general appearance of the spectrum and the weak intensity of the band at 550 nm are characteristic of octahedral stereochemistry[21]. The iron complexes have bands around 530-550 nm. The intense red colour of the compounds points to electron-transfer from metal to ligand[22-24]. The reflectance spectrum of the deprotonated Ni(II) complex shows bands at 510 (b) and 570 (sh) nm, indicative of square-planar arrangement around nickel possessing the chromophore, NiN_4[25-27].

All the copper complexes with nondeprotonated diamide show a typical broad band around 600-700 nm characteristic of distorted octahedral structures. In the deprotonated diamide copper complex (type-b), the absorption maximum shifts to 460 nm. The low value of λ_{max} indicates a remarkable degree of tetragonal distortion[28]. The spectra are similar to those of the complexes of picolinamide[4] and pyrazine-2-amide[3] and are quite different from those of the ionic complexes where coordination occurs through N, N donors in the deprotonated complex and through N, O donors in the non-deprotonated ones. The copper complex (type-c) has a typical broad band around 700-800 nm suggestive of a distorted octahedral structure. The nondeprotonated nickel complexes have bands around 620-650 nm and the spectra resemble the diffuse reflectance spectrum of the Ni(II) complex with 8-quinoline carboxamide[29]. It is possible, therefore, that coordination likewise takes place through amide oxygen and pyrazine ring nitrogen.

To get further insight into the nature of bonding[30], ESR spectra of the Cu(II) complexes were recorded in the powder form at liquid N_2 temperature: the Cu $(Pzda)_2(ClO_4)_2$ compound[7] whose crystal structure is known[31,32] was also subjected to ESR analysis under the same conditions for comparison. Unfortunately the ESR spectra for the perchlorate and nitrate complexes are isotropic and little structural information can be gained from these. The $Cu(Pzda\text{-}H)_2$ compound gives a reversed axial spectrum; however, it has been observed[33] that an axially reversed ESR spectrum can occur for a $d_{x^2-y^2}$ ground state rather than a d_{z^2} ground state if there are inequivalent sites within a unit cell. Therefore, additional evidence must be sought to fully understand the observed reversed spectrum. The $Cu(Pz\text{-}3\text{-}CONH_2\text{-}2\text{-}COO)_2.4H_2O$ complex shows typical axial spectrum indicating tetragonally distorted complex with $d_{x^2-y^2}$ ground state having $g_{\parallel} > g_{\perp}$. The observed g value (2.28) is close to the values found for CuO_2N_2 chromophores present in copper-glycinate[34] 8-hydroxyquinolinate complexes[35].



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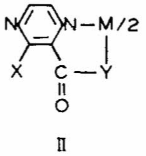

II

M = Cu, X = H, Y = O; M = Cu, X = $CONH_2$, Y = NH; M = Ni, X = H, Y = NH.

From the results of elemental analyses, visible and infrared spectra and magnetic measurements it appears that bis(pyrazine-2-amide)-$MnCl_2$, -$FeCl_2$ complexes and the bis(diamide)-$CoCl_2$ complex have halogen bridged infinite chain structures[36]. The diamide-$CuCl_2$ is presumed to have the structure(I) where both $CONH_2$ groups take part in coordination. In the case of $Fe(ClO_4)_2$-bis(pyrazine-2-amide) complex, since infrared evidence suggests the presence of ionic perchlorate, octahedral structure is presumed to occur via additional bonding through free nitrogen atoms of adjacent pyrazine rings of neighbouring molecules.

The deprotonated complexes of Cu(II) and Ni(II) may be represented by structure(II).

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