Indian Journal of Chemistry
Vol. 22A, April 1983, pp. 307-310

# Metal Complexes of Pyridine-2-amidoxime

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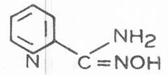
*Received* 4 *September* 1982; *revised and accepted* 27 *December* 1982

Complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with pyridine-2-amidoxime have been prepared and characterised. Ni(II) forms two types of complexes: (i) a diamagnetic square planar complex with deprotonated ligand; and (ii) paramagnetic pseudooctahedral complexes with the free ligand. Bonding in all the complexes takes place via nitrogen atoms of pyridine ring and the oxime group.

Although investigations of metal complexes with oximes of heterocyclic origin have been extensive, studies on metal complexes with amidoximes are rather limited[1-3], being mostly analytical in nature[4-8]. Amidoximes are known to possess biological activity[9-12]. In view of little work on metal complexes of amidoximes and interesting biological activities exhibited by these potential ligands, it was considered worthwhile to study metal complexes of pyridine-2-amidoxime. Presently Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) complexes of pyridine-2-amidoxime (I) have been prepared and characterised on the basis of elemental analyses, magnetic moment measurements and IR and electronic spectral data.




Pyridine-2-amidoxime

I

## Materials and Methods

The metal salts used were of BDH(AR) or Merck (GR) grade, except the bromides and perchlorates which were prepared in the laboratory. Pyridine-2-amidoxime (I) was prepared according to Bernasek[13].

*Preparation of metal complexes*—The complexes were prepared by refluxing a mixture of ethanolic solutions of the ligand and metal salts [iron (II) salts were, however, added as solids to the ligand solution; $N_2$ atmosphere was maintained for complexes of cobalt nitrate, perchlorate and iron (II) salts]. The reaction mixture was concentrated and cooled when crystals of the complexes separated out. However, in the case of cobalt nitrate, cobalt perchlorate and nickel perchlorate ether was added to the reaction mixture followed by scratching to effect crystallisation. The following purification procedures were adopted: (i) the solid nickel perchlorate complex was repeatedly refluxed with dry benzene and filtered; (ii) the crude, solid complexes of cobalt nitrate and cobalt perchlorate were dissolved in ethanol and reprecipitated by adding ether; and (iii) the other solid complexes were washed with ethanol.

The complexes obtained as crystalline solids after filtration were dried *in vacuo* over $CaCl_2$.

The deprotonated nickel complex was prepared by keeping on a steam-bath an aqueous solution containing nickel chloride and the ligand previously neutralised with sodium hydroxide and filtering off the resulting reddish brown precipitate, washing with hot water and drying as before.

In all these preparations 1:2 mol ratio (metal : ligand) was used.

Analyses, magnetic and spectral measurements were made as described elsewhere[14].

## Results and Discussion

The analytical, conductance and magnetic moment data of the complexes are given in Table 1.

*Conductivity data*—In methanol the complexes behave as uni-bivalent electrolytes (the manganese complex is, however, uni-univalent) whereas in dry nitromethane, the conductance values, except for the perchlorate complexes, are considerably less and occur between non-electrolyte and uni-univalent electrolyte types implying that anions are coordinated in the solid state and that in methanol complete replacement of anions by the solvent takes place. The perchlorate complexes are ionic or at best weakly coordinated. Because of solubility limitations/decomposition, conductances of the bromide and nitrate complexes of copper have been measured in aqueous solution and behave as uni-bivalent electrolytes. The somewhat larger values in aqueous medium may be ascribed to an equilibrium of the type indicated by Blackmore *et al.*[15]. The conductance of copper chloride complex in nitromethane ($1 \times 10^{-4}$ *M*) indicates that chloride is ionic.

Table 1—Elemental Analyses, Magnetic Moments and Conductances of Metal Complexes of Pyridine-2-amidoxime(L)

| Complex | Colour | $\mu_{eff}$ (B.M.) at 27°C | Metal (%) Calc. | Metal (%) Found | Anion (%) Calc. | Anion (%) Found | N (%) Calc. | N (%) Found | $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$) Methanol | $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$) Nitro-methane |
|---|---|---|---|---|---|---|---|---|---|---|
| $CuL_2Cl_2$ | Bright green | 1.82 | 15.50 | 14.91 | 16.77 | 17.60 | 20.50 | 20.07 | 218.7 | 146.4 |
| $CuL_2Br_2$ | Do | 1.82 | 12.80 | 12.61 | 32.00 | 32.41 | 16.80 | 17.20 | 331.3* | — |
| $CuL_2(NO_3)_2$ | Green | 1.77 | 13.76 | 13.90 | — | — | 24.12 | 24.07 | 238.0* | — |
| $CuL_2(ClO_4)_2$ | Do | 1.70 | 11.80 | 13.19 | — | — | 15.60 | 15.10 | — | — |
| $NiL_2Cl_2$ | Greenish blue | 3.21 | 14.44 | 13.77 | 17.50 | 17.15 | 20.80 | 20.66 | 184.8 | — |
| $NiL_2Br_2$ | Do | 3.23 | 12.00 | 12.65 | 32.40 | 33.43 | 17.04 | 17.64 | 192.0 | — |
| $NiL_2(NO_3)_2$ | Light blue | 2.99 | 12.98 | 12.45 | — | — | 24.50 | 23.68 | 198.2 | 64.1 |
| $NiL_2(ClO_4)_2$ | Dirty white | 3.27 | 11.09 | 10.75 | — | — | 15.80 | 15.91 | 220.3 | 162.5 |
| $Ni(L-H)(OH)H_2O$ | Dark brown | Dia- | 25.56 | 25.38 | — | — | 18.28 | 19.35 | — | — |
| $CoL_2Cl_2$ | Brown | 4.74 | 14.60 | 14.43 | 17.58 | 17.69 | 20.80 | 20.70 | 158.3 | — |
| $CoL_2Br_2$ | Do | 4.43 | 11.97 | 11.86 | 32.40 | 32.96 | 17.04 | 16.69 | 224.1 | 73.2 |
| $CoL_2(NO_3)_2 2H_2O$ | Do | 1.75 | 11.92 | 10.84 | — | — | 22.63 | 22.52 | — | 35.5 |
| $CoL_2(ClO_4)_2$ | Do | 2.64 | 11.09 | 10.61 | — | — | 15.78 | 15.82 | — | 131.0 |
| $FeL_2Cl_2$ | Orange red | 5.35 | 13.92 | 14.24 | 17.80 | 17.26 | 20.85 | 19.84 | 174.3 | 49.5 |
| $Fe(L-H)ClO_4H_2O$ | Black | 2.08 | 18.10 | 17.86 | — | — | 13.58 | 13.95 | — | 73.2 |
| $MnL_2Cl_2$ | Yellow | 5.88 | 13.68 | 13.50 | 17.60 | 17.19 | 20.90 | 19.90 | 110.9 | — |

*In water.

*Magnetic moments*—All the copper complexes have moments in the region 1.70-1.82 B.M. indicating square planar/octahedral geometry for Cu(II) complexes[16], nickel complexes have magnetic moments in the range 2.99-3.27 B.M., characteristic of octahedral structure. The deprotonated nickel complex is diamagnetic and, therefore, has a planar structure. The magnetic moments of the cobalt complexes, particularly the nitrate and perchlorate complexes, are subnormal, for octahedral, stereochemistry. There are several factors[17], which may contribute to this, but in the absence of low temperature magnetic moments it is difficult to discuss the significance of this behaviour.

The iron (II) chloride complex has a moment characteristic of octahedral structure usually assigned to spin free states[18]. The iron (II) perchlorate complex has, however, a lower magnetic moment and in the absence of temperature dependent magnetic study, it is difficult to arrive at a conclusion. The manganese(II) complex is of high spin type having a close-to-spin-only value and this occurs irrespective of whether the ligand environment is octahedral, tetrahedral or has a lower symmetry[19].

*Infrared spectra*—The infrared spectra of the complexes and the free ligand have been recorded and the assignments are based on the interpretations advanced for a number of amidoximes[20,8] as well as pyridine-2-aldoxime[21].

The spectrum of the free ligand exhibits two sharp bands at 3356 and 3472 $cm^{-1}$, which may be assigned to $\nu_{as}$ $NH_2$ and $\nu_s$ $NH_2$ respectively. A broad band in the region 3180-2970 may be due to associated $\nu$OH and $\nu NH_2$. Another broad band in the region 2850-2745 $cm^{-1}$ may be due to $\nu$OH (free) involved in strong hydrogen bonding. The band at 1633 $cm^{-1}$ has been assigned[22] to $\nu C=N$ and the one appearing at 950 $cm^{-1}$ to $\nu N-O$ (see ref. 23).

In all the complexes, the $\nu N-O$ of the free ligand is shifted ($\Delta\nu$ 50-60 $cm^{-1}$) to higher wavenumbers and appears ~1010-1020 $cm^{-1}$; the deprotonated nickel complex suffers a greater shift, in harmony with the nitrone structure produced thereby[24]. The shift of $\nu N-O$ to higher wave numbers indicates coordination of metal ion through oxime nitrogen. The bonding is compatible with the preferred mode of coordination for oximes[25].

In general, only small shifts in the vibrational frequencies of the pyridine rings are observed on complex formation. However, evidence of coordination of the pyridine ring nitrogen is manifested in the changes in in-plane and out-of-plane ring deformation modes at 620 and 440 $cm^{-1}$ respectively in free ligand, showing positive shift of 15-20 $cm^{-1}$ in the complexes indicating participation of heterocyclic ring nitrogen in coordination[26].

The infrared spectra of the cobalt chloride and nickel chloride complexes are similar as also those of the manganous chloride and the cobalt bromide implying same coordination sites. The iron (II) chloride complex also shows similarity with the manganese (II) chloride complex in 1300-600 $cm^{-1}$ region although dissimilarity exists in 400-1400 $cm^{-1}$ region and particularly in the appearance of a broad band around 3500-3000 $cm^{-1}$. The complex of iron (II) perchlorate shows a broad band in 3500-3000 $cm^{-1}$

region, similar to that shown by cobalt nitrate complex, indicating presence of water[27], probably coordinated (although bands attributed to coordinated water[28] are not easily discernible from the spectra due to ligand interference). This is supported by insignificant loss in mass on heating the complexes in an air oven at $110 \pm 5$°C. However, this remains inconclusive in view of previous reports[29] particularly when the ligand is capable of forming hydrogen-bond with water.

The spectra of the complexes exhibit splittings around 810-850 and 1300-1380 $cm^{-1}$ in the case of nitrate complexes of copper and nickel, and ~1100 $cm^{-1}$ for the perchlorate complexes of iron and nickel. These together with their $\Lambda_M$ data suggest semi-coordination of oxyanions[30] (the observed $\Lambda_M$ for the nickel perchlorate complex is probably due to solvolysis). The nitrate in the complex of cobalt nitrate is ionic, its low $\Lambda_M$ in nitromethane may be ascribed to the presence of nitrate groups in the coordination sphere as a result of exchange under the influence of the solvent. The perchlorates in the complexes of copper and cobalt are weakly coordinating/ionic.

*Electronic spectra*—The spectra of the complexes in solid state and solution spectra of those soluble in solvents of interest have been recorded. In aqueous medium the spectra of all the copper complexes are identical with band maxima ~15000 $cm^{-1}$, implying similar coordination environment. A saturated solution of copper chloride complex in nitromethane gives rise to a broad band with maximum centered ~14500 $cm^{-1}$. The mull spectra of the copper complexes exhibit two or three maxima between 14000 and 18000 $cm^{-1}$ indicative of square planar structures[31-33]. The spectra of the various nickel complexes in methanol are almost identical but differ from those taken in nitromethane as well as in the solid state, evidently owing to solvolysis. The mull spectra of the nickel complexes with the free ligand display two maxima in the regions 10500-11000 $cm^{-1}$ ($\nu_1$), 16000-18000 $cm^{-1}$ ($\nu_2$). These have been tentatively assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and $\rightarrow {}^3T_{1g}$ transitions respectively; the $\nu_2/\nu_1$ values are in the expected range, in agreement with their octahedral structures[34]. The reflectance spectrum of the deprotonated nickel complex has a broad band with maximum ~20,000 $cm^{-1}$ indicative of square planar geometry having a singlet ground term ${}^1A_{1g}$(ref. 35).

The spectra of the cobalt complexes are not well characterised. The complexes of both cobalt nitrate and perchlorate do not exhibit any well resolved absorption maxima in the region 25,000-12,500 $cm^{-1}$ both in the solid state as well as in nitromethane and identification of cobalt(II) species therein, therefore, remains inconclusive. The solid state spectra of cobalt chloride and bromide complexes exhibit two/three maxima in the region 17,500-20,000 $cm^{-1}$; the cobalt bromide complex in nitromethane shows a shoulder ~19600 $cm^{-1}$ due to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ in addition to a strong peak at 24690 $cm^{-1}$ suggestive of the presence of cobalt (II) species in an octahedral environment. It may be that in the nitrate and perchlorate complexes the concentration of cobalt (II) species is too low (through oxidation by the ligand[36] and/or air) to exhibit any maxima in the region studied. The presence of cobalt (III) species in the complexes, however, could not be confirmed from the UV spectra, in aqueous solution, of the ligand and the complexes. The absorption maximum of the free ligand occurring ~35700 $cm^{-1}$ is seen to shift to higher energy and appears in the region 38500-37000 $cm^{-1}$ in the complexes.

The complexes of iron (II) chloride and perchlorate in nitromethane give high intensity absorption in the region 20000-23000 $cm^{-1}$, owing possibly to the presence of $-N=C-C=N-$ grouping. The α-diimine function is known[37] to undergo an allowed metal→ligand charge transfer transition at low energy. The iron(II) perchlorate complex in nitromethane shows weak absorptions at ~8700 and 10,420 $cm^{-1}$ assignable to ${}^5T_{2g} \rightarrow {}^5E_g$ (*D*) indicating octahedral geometry around the metal ion; the doublet may be attributed to a dynamic Jahn-Teller effect[35]. The manganese (II) compound exhibits in the visible region only a weak shoulder usually attributed to *d-d* transition arising out of the presence of a distorted octahedron.

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