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Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) COMPLEXES OF ACETIC ACID AND PHENYL ACETIC ACID HYDRAZONES OF 2- AMINONICOTINALDEHYDE

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Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) complexes of tridentate Schiff base ligands derived from the condensation of acetic acid hydrazides, with 2-aminonicotinaldehyde have been synthesized. These complexes have been characterized based on analytical, molar conductance, magnetic susceptibility, thermal, electronic and ESR spectral studies.

INTRODUCTION

2-Aminonicotinaldehyde having comparable groups to that of salicylaldehyde and 2-aminobenzaldehyde was not investigated very well for synthesis of Schiff bases and their metal complexes. A number of reviews on Schiff base metal complexes derived from salicylaldehyde and 2-aminobenzaldehyde are available[1-4]. Only recently some Schiff bases of 2-aminonicotinaldehyde were reported[5,6]. In the present investigation we report preparation and characterization of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pd(II) complexes of acetic acid hydrazone of 2- aminonicotinaldehyde (AHANA) and phenyl acetic acid hydrazone of 2-aminonicotinaldehyde (PAHANA). These Schiff bases act as neutral tridentate with NNO donor set or bidentate with NN donor set.

EXPERIMENTAL

Acetic acid and phenyl acetic acid hydrazones of 2- aminonicotinaldehyde were prepared as reported earlier[5] by refluxing ethanolic solution of equimolar quantities of 2-aminonicotinaldehyde and acetic acid hydrazide or phenyl acetic acid hydrazide, the yellow crystalline products precipitated were filtered, washed with ethanol and ether and dried in vacuo. The compounds were recrystallized from hot ethanol. All other chemicals used were of analytical grade and the solvents were purified before use.

Preparation of Complexes

Co(II), Ni(II) and Cu(II) Complexes: Solution of hydrated metal halide (1 mmol) and the ligand (1 mmol) in 50 ml of ethanol was shaken for 1/2 hr in the case of copper and 2 hrs in the case of cobalt and nickel. Crystals of the complexes separated were filtered, washed with ethanol and ether and dried.

Zn(II) and Cd(II) Complexes: The hydrated metal chloride (1 mmol) dissolved in minimum amount of ethanol was added to ligand (1mmol) dissolved in 25 ml of ethanol; the complexes precipitated immediately were filtered, washed with ethanol and ether and dried.

Pd(II) Complexes: $[(NH_4)_2Pd]Cl_4$ (1 m mol) in 10 ml of ethanol was added to the ligand (1 mmol) dissolved in 25 ml of ethanol. The yellow complex precipitated immediately was allowed to stand for 1/2 hr and filtered, washed with ethanol and ether and dried.

RESULTS AND DISCUSSION

All the complexes are coloured, stable in air and have decomposition temperatures in the range of 205-260°C. All the complexes are insoluble in common organic solvents, but soluble in DMF and DMSO. The molar conductance of these complexes (10–16 mhos cm^2mol^{-1}) in DMF (10 M) show their non- electrolytic nature[7]. The analytical data suggest the compositions of complexes to be $ML(H_2O)X_2$ (M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), L = Ligand, X = Cl or Br) and MLX (M = Pd, X = Cl).

In the IR spectra of ligands[5,8] there are two sharp bands in the region of 3225–3380 cm^{-1} corresponding to ν(N–H) of amine group of pyridine ring. These two bands are shifted to lower region of 3200–3280 cm^{-1} indicating that the $-NH_2$ group on pyridine ring is coordinated to metal[8]. The amide carbonyl band ν(C=O) located in the region 1650–1675 cm^{-1} and ν(C=N) of azomethine located in the region 1615–1630 cm^{-1} are shifted to lower regions of 1640–1665 cm^{-1} and 1590–1610 cm^{-1} respectively indicating involvement of amide carbonyl group, and azomethine group in the coordination[9]. In addition to these, in Co(II), Ni(II) Cu(II), Zn(II) and Cd(II) complexes there is a new broad band in the complexes, in the region of 3420–3510 cm^{-1} corresponding to water molecule associated with the complexes. the amide carbonyl band of ligand remains unchanged in the spectra of Pd(II) complexes but the azomethine band of ligand undergoes shift to lower wave numbers by 30 cm^{-1}, indicating that the amide carbonyl oxygen is not involved in the coordination[9]. Thus in the case of palladium the ligands act as bidentate coordinating through nitrogen of $-NH_2$ on pyridine ring and azomethine. The new bands appearing in the 275–320 cm^{-1}, 380–460 cm^{-1} and 480–520 cm^{-1} region in the complexes may tentatively be assigned to ν(M–Cl), ν (M–O) and ν(M–N) modes respectively[9, 10].

Thermogravimetric analyses of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes show a mass loss equivalent to one mole of water molecule in the region of 210–260°C indicating coordination of a water molecule[11]. This is further confirmed by one endothermic peak in DT analysis.

The room temperature magnetic moment values (Table 1) obtained for Co(II), Ni(II) and Cu(II) complexes indicate that they are high-spin and are octahedral[12]. But the μ_{eff} values reported for these complexes are slightly higher than the spin-only values of respective metal ions. The ground terms of Co(II) ion in octahedral geometry is $^4T_{2g}$ which is orbitally degenerate. This makes an orbital contribution to the magnetic moment. The high-spin Ni(II) and Cu(II) in an octahedral geometry have ground terms $^3A_{2g}$ and ^2E_g respectively, which have no orbital contribution. However $^3A_{2g}$ of Ni(II) and ^2E_g of Cu(II) mix up with higher levels $^3T_{2g}$ and $^2T_{2g}$ respectively, which have orbital angular momentum. Thus to the extent of spin-orbit coupling μ_{eff} values are higher than spin-only values.

TABLE 1

MAGNETIC AND ELECTRONIC SPECTRAL DATA AND VARIOUS LIGAND FIELD PARAMETERS OF COMPLEXES

Complex	μ_{eff}	ν_1 (cm^{-1})	ν_2 (cm–1)	ν_3 (cm^{-1})	ν_2/ν_1 (cm^{-1})	10 Dq (cm^{-1})	B' (cm^{-1})	β
$Co(AHANA)(H_2O)Cl_2$	4.92	8670	18350	21150	2.12	9610	689	0.62
$Co(PAHANA)(H_2O)Cl_2$	4.86	8720	18660	21500	2.14	9715	670	0.60
$Ni(AHANA)(H_2O)Cl_2$	3.08	9530	15540	25920	1.63	11650	932	0.86
$Ni(PAHANA)(H_2O)Cl_2$	3.12	9600	15745	26325	1.64	11800	908	0.84
$Cu(AHANA)(H_2O)Cl_2$	1.82	—	16130	—	—	16130	—	—
$Cu(PAHANA)(H_2O)Br_2$	1.80	—	15750	—	—	15750	—	—
$Cu(PAHANA)(H_2O)Cl_2$	1.86	—	16660	—	—	16660	—	—
$Cu(PAHANA)(H_2O)Br_2$	1.82	—	16130	—	—	16130	—	—
$Pd(AHANA)Cl_2$	Dia	17450	25100	—	—	—	—	—
$Pd(PAHANA)Cl_2$	Dia	17730	26135	—	—	—	—	—

The electronic spectral data of complexes are shown in Table 1. The electronic spectra of Co(II) and Ni(II) complexes show three spin allowed bonds characteristic of octahedral geometry[13]. Co(II) complexes show three bands in the regions of 8670–8720 cm^{-1}, 18380–18660 cm^{-1} and 21150–21500 cm^{-1} corresponding to transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)(\nu_3)$, respectively. The Ni(II) complexes show three bands in the regions of 9530–9600 cm^{-1}, 15540–15745 cm^{-1} and 25920–26315 cm^{-1} corresponding to transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$, $^4A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_3)$, respectively. The octahedral geometry of Co(II) and Ni(II) complexes is further supported by the ratio ν_2/ν_1 which lie around 2.16 and 1.62 respectively. Various ligand field parameters like ligand field splitting energy (10 Dq), Racah-inter-electronic repulsion parameter B' and the nephelauxetic ratio $\beta(=B'/B)$ of the Racah values for the complex (B') and the free ion (B) have been calculated. The B-values for the complexes are lower than the free ion values (B) indicating overlap of metal and ligand orbitals and delocalization d-electrons. On increasing the delocalization, β-values decrease and become less than unity. The β–values can be used as an index of covalent complexing power[14]. The calculated β-values are less than one suggesting considerable amount of covalent character in the metal-ligand band. The electronic spectra of Cu(II) complexes show a broad band in the region of 15750–16660 cm^{-1} corresponding to spin-allowed transition $^2E_g \rightarrow {}^2T_{2g}$ characteristic of tetragonally distorted octahedral Cu(II) complexes[13,15]. The electronic spectra of Pd(II) complexes exhibit two bands in the regions of 17450–17730 cm^{-1} and 25100–16136 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ respectively. These two bands are characteristic of square-planar geometry in palladium complexes[13].

The ESR spectra of polycrystalline Cu(II) complexes at room temperature are anisotropic and show two bands corresponding to $g_{\parallel}$ and $g_{\perp}$ with no resolution.

In all the Cu(II) complexes it has been found that $g_{\|} > g_{\perp}$. The ESR spectra of

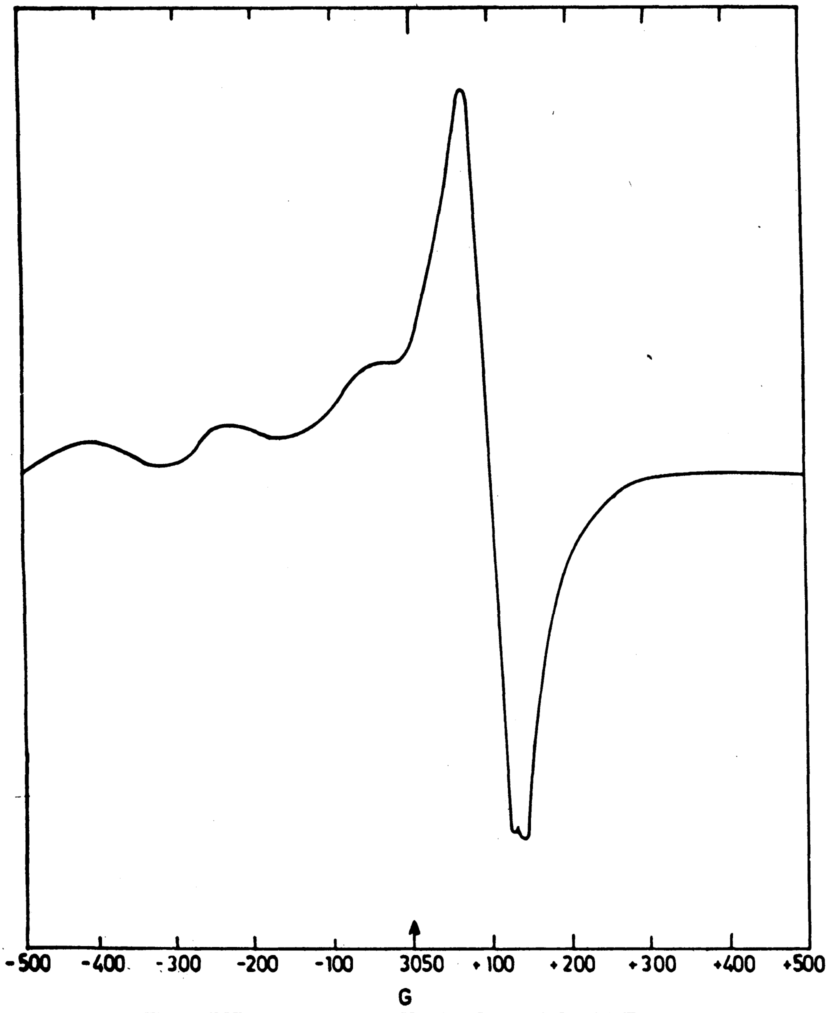


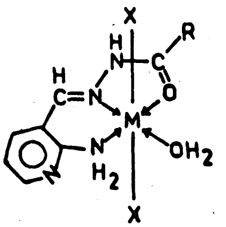
Fig. 1 ESR spectra of Cu(AHANA)Cl_2(H_2O)] at LNT.

Cu(AHANA)(H_2O)Cl_2 (Fig. 1), Cu(AHANA)(H_2O)Br_2 and Cu(PAHANA)(H_2O)Cl_2 in DMF solution at liquid N_2 temperature show three clear bands in the $g_{\|}$ region with the fourth band partially hidden under more intense $g_{\perp}$ band. From these well resolved bands the copper hyperfine splitting constants $A_{\|}^{Cu}$ have been calculated. The $g_{\perp}$ region is not very well resolved, the copper hyperfine splitting cought $A_{\perp}^{Cu}$ have been calculated by taking one third of line widths at half maximum16. The values of $g_{\|}$, $g_{\perp}$, g_0, $A_{\|}^{Cu}$, $A_{\perp}^{Cu}$ and A_0^{Cu} are presented in Table 2. The $g_{\|}$ and $g_{\perp}$ values of the Cu(II) complexes are in the range of 2.207–2.220 and 2.042-2.049. The fact that $g_{\|} > g_{\perp}$ is consistent with the elongated tetragonal stereochemistry and indicates that the unpaired electron is in the $d_{x^2-y^2}$ ground state orbital[17]. The information regarding the nature of metal-ligand bonding can be obtained from $g_{\|}$ values[18]. $g_{\|}$ is normally 2.3 or larger for ionic and less than 2.3 for covalent environment. Since the $g_{\|}$ values found for Cu(II) complexes are less than 2.3, it indicates that the metal-ligand bonds are covalent. $A_{\|}^{Cu}$ and$A_{\perp}^{Cu}$ values of the complexes are in the range of 180–187 × 10^{-4} cm^{-1} and 13–19 × 10^{-4} cm^{-1} respectively, and these values are well with in the range expected for tetragonally distorted Cu(II) complexes[19, 20].

TABLE 2
ESR SPECTRAL DATA OF Cu(II) COMPLEX

ESR parameter	$Cu(AHANA)H_2OCl_2$	$Cu(AHANA)H_2OBr_2$	$Cu(PAHANA)H_2OCl_2$
$g_{\|}$	2.212	2.220	2.207
$g_{\perp}$	2.044	2.049	2.042
g_0	2.100	2.106	2.097
$A_{\|}^{Cu} \times 10^{-4}\ cm^{-1}$	187	186	180
$A_{\perp}^{Cu} \times 10^{-4}\ cm^{-1}$	16	13	19
$A_0 \times 10^{-4}\ cm^{-1}$	73.00	70.66	72.50
α^2	0.78	0.80	0.76
α'^2	0.30	0.28	0.33
β^2	0.65	0.64	0.67
v^2	0.52	0.55	0.52
$K_{\|}^2$	0.51	0.51	0.51
$K_{\perp}^2$	0.41	0.44	0.40
$\lambda\ (cm^{-1})$	649	662	629

The orbital reduction coefficents such as $\alpha^2, \alpha^{1^2}, \beta^2, v^2, K_{\|}^2,$ $K_{\perp}^2$ and the spin-orbit coupling constant λ has been calculated[21, 22] and presented in the Table 2. α^2 values are in the range of 0.76–0.80 indicating the presence of appreciable in-plane σ-covalency $K_{\|}^2 > K_{\perp}^2$ indicates that there is large out-of-plane pi-bonding and little in-plane pi-bonding[18]. The calculated λ values for the Cu(II) complexes are in the range of 629–662 cm^{-1}. These values are much lower than the free ion value λ_0 (828 cm^{-1}) indicating considerable mixing of ground and excited terms.



M = Co(II), Ni(II), Cu(II)
Zn(II), cd(II)
X = Cl / Br
R = $-CH_3$ (AHANA)
R = $-CH_2-C_6H_5$ (PAHANA)

Fig. 2 Structure of complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Based on the above results and discussions octahedral structures have been assigned to Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes (Fig. 2) and square-planer structure to Pd(II) complexes (Fig. 3).

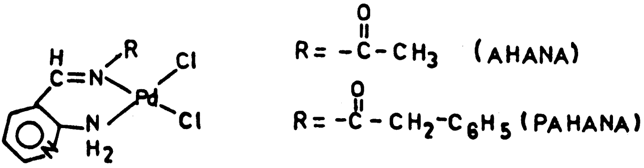


Fig. 3. Structure of Pd(II) complex.

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REFERENCES

1. N.F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
2. V.L. Goedken, N.K. Kildahl and D.H. Busch, *J. Coord. Chem.* **7**, 89 (1977).
3. R.D. Jones, D.A. Summerville and F. Basalo, *Chem. Rev.*, **79**, 139 (1979).
4. B.M. Higson and E.D. Mckenzie, *J. Chem. Soc. Dalton*, 269 (1977).
5. K. Mogilaiah, K. Vijayender Reddy and B. Srinivasulu, *J. Indian Chem. Soc.*, **62**, 259 (1985).
6. K. Mogilaiah, G. Rama Rao, B. Swamy and B. Srinivasulu, *Sulfur Letters,* **8**, 229 (1988).
7. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
8. G.R. Burns, *Inorg. Chem.*, **7**, 277 (1968).
9. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York 1978.
10. R.C. Paul, R.S. Chopra, and G. Singh, *Inorg. Chim. Acta.*, **14**, 105 (1963).
11. D. Venkateswar Rao, N. Rama Rao and M.C. Ganorkar, *Indian J. Chem.*, **27A**, 73 (1988).
12. B,N. Figgis and B.N. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1964).
13. A.B.P. Lever, Inorganic Electronic Spectroscopy Elsevier, Amsterdam (1968).
14. T.M. Dunn, Modern Coordination Chemistry, Edited by J. Lewis and R.G. Wilkins, Interscience, New York, p.267 (1960).
15. Y. Nishida and S. Kida, *Coord. Chem. Rev.*, **27**, 275 (1979).
16. P.S. Zacharias, J. Mary Elizabathe and A. Ramachandraiah, *Indian. J. Chem.*, **23A**, 26 (1984).
17. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
18. D. Kivelson and R. Neiman, *J. Chem. Phys.*, **35**, 149 (1961).
19. Y. Murakami, Y. Matsuda and K. Sakata, *Inorg. Chem.*, **10**. 1734 (1971).
20. G.F. Kokosziza, *J. Phys. Chem.*, **71**, 121 (1967).
21. A.H. Maki and B.R. McGarvery, *J. Chem. Phys.*, **29**, 31 (1958).
22. A. Syamal, *Chemical Education*, 26 (1988).

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