

Characterisation of (2+2) Macrocylic Compounds of Co(II) and Ni(II) Derived from 2,6-Diacetyl Pyridine and Phenylene Diamines

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A number of complexes of the types $[ML_1]X_2$, $[ML_2]X_2$ [$M = Co(II)$ or $Ni(II)$; $X = Cl^-$, Br^- , NO_3^- , OAc^- ; $L_1 = Bis(2,6-diacetylpyridine-1,3-diamine)$ and $L_2 = Bis(2,6-diacetylpyridine-1,4-diamine)$] have been synthesised and characterised.

INTRODUCTION

Considerable efforts have been made to study the synthesis, physico-chemical and physiological activities of tetra-, penta- and hexa-aza-macrocylic compounds formed by Schiff base condensation reaction between carbonyl compounds and mono-, di- and tri-amines which have attained an important place in the preparation of synthetic compounds¹⁻⁴. As such their preparation involves a number of factors. A particularly useful precursor dicarbonyl is 2,6-diacetyl pyridine which has a good nitrogen donor atom in the pyridine ring. The primary amines employed for condensation reactions were 1,3 and 1,4-diamino benzene giving rise to 20- and 22-membered rings around the template ions respectively. Any attempt to isolate the macrocylic ligands of varying ring size has become unsuccessful due to destabilisation of the ring formed in absence of the metal ion as template.

In all cases, the macrocycles were prepared by reacting 2,6-diacetyl pyridine (DAP) with the appropriate diprimary amine in equimolecular proportion (2 + 2) in presence of metal adopting *in situ* procedure. It was investigated during its preparation that in absence of metal ion only viscous oils were obtained. It appears, therefore, that the metal ion has a stabilising effect on the macrocycle. We could isolate eight macrocylic complexes with the ligands L_1 and L_2 in good yield and well crystalline form.

EXPERIMENTAL

All the chemicals used in the present study were from BDH of reagent grade. The 2,6-diacetyl pyridine, *m*- and *p*-phenylene diamine obtained from Aldrich (USA) were used without further purification.

Bis(2,6-diacetylpyridine-1,4-diaminobenzene)

$M(II)X_2$; $[ML_2]X_2$: $M = Co(II)$, $Ni(II)$; $X = Cl^-$, Br^- , NO_3^- , OAc^-

Hydrated metal(II) salt (.005 mole) was dissolved in 20 mL absolute alcohol

and a warm alcoholic solution of *p*-phenylene diamine (0.01 mol) was added slowly with constant stirring. The colour of the solution became blackish. The whole mixture was refluxed on water bath for 1 h. On cooling, a blackish substance was obtained and all the solvent was evaporated in two days. The residue was first crystallised with alcohol and then washed with alcohol, ether and dried *in vacuo*.

Bis(2,6-diacetylpyridine-1,3-diaminobenzene)

M(II) X₂; [ML₁]X₂: M = Co(II), Ni(II); X = Cl⁻, Br⁻, NO₃⁻, OAc⁻

0.01 mole of 2,6-diacetylpyridine was dissolved in 20 mL absolute alcohol on warming. It was added slowly to an alcoholic solution of hexahydrated metal salt (0.005 mol) with stirring. To this solution, an alcoholic solution of 1,3-diaminobenzene (0.001 mole) was added slowly with constant stirring. The whole mixture was refluxed on water bath for 1 h. A blackish colour residue in both cases was isolated after cooling. It was washed with alcohol/ether and dried *in vacuo*.

TABLE-1
ANALYTICAL DATA OF Co(II) AND Ni(II) COMPLEXES

Compound	Yield (%)	%, Found (Calcd.)				Anion
		M	C	N	H	
1. [CoL ₁]Cl ₂	80	9.65 (9.73)	59.50 (60.06)	13.85 (14.01)	4.15 (4.36)	10.96 (11.84)
2. [CoL ₁](NO ₃) ₂	85	8.34 (8.94)	54.95 (55.18)	16.98 (17.16)	3.54 (3.98)	—
3. [CoL ₂]Cl ₂	75	9.42 (9.73)	59.80 (60.06)	13.85 (14.01)	4.12 (4.33)	11.54 (11.84)
4. [CoL ₂](NO ₃) ₂	80	8.54 (8.94)	54.75 (55.18)	16.84 (17.16)	3.54 (3.98)	—
5. [NiL ₁]Cl ₂	82	9.54 (9.78)	59.35 (60.03)	13.75 (14.00)	4.10 (4.33)	11.50 (11.83)
6. [NiL ₁](NO ₃) ₂	85	8.45 (8.99)	54.75 (55.15)	16.75 (17.15)	3.46 (3.98)	16.35 (16.55)
7. [NiL ₂]Cl ₂	80	9.25 (9.78)	59.36 (60.03)	13.46 (14.00)	4.15 (4.33)	11.54 (11.83)
8. [NiL ₂](NO ₃) ₂	80	8.44 (8.99)	54.75 (55.15)	16.75 (17.15)	3.45 (3.98)	—

L₁ = bis(2,6-diacetylpyridine-1,3-diaminobenzene.)

L₂ = bis(2,6-diacetylpyridine 1,4-diaminobenzene.)

RESULTS AND DISCUSSION

The analytical data of the complexes are given in Table-1.

The infrared spectra have been recorded on Perkin-Elmer spectrophotometer at Bose Institute, Calcutta and given in Table-2. The spectra of metal complexes which fall within the vicinity of 1600 cm⁻¹ are attributed to ν(C=N) and pyridine

ring vibratious. In fact the $\nu(\text{C}=\text{N})$ occurs in the proximity of 1625 cm^{-1} to 1615 cm^{-1} in metal complexes whereas it was expected to fall within the range $1700\text{--}1650\text{ cm}^{-1}$. The low value in certain cases is suggestive of the coordination of N-donor atom of azomethine linking with the metal centre⁵. In addition to these bands two more bands were observed in their spectra^{6,7} which may be assigned to pyridine ring vibration. These bands appear between $640\text{--}615$ and $435\text{--}422\text{ cm}^{-1}$. These values higher than ligands revealed that pyridine nitrogen is involved in complexes. A pair of bands in the vicinity of $2924\text{--}2910\text{ cm}^{-1}$ and $2856\text{--}2850\text{ cm}^{-1}$ were located and have been assigned to $\nu(\text{C}\text{--}\text{H})$ vibrations. The spectra show bands between $1365\text{--}1350\text{ cm}^{-1}$ which may be assigned to --CH_3 deformation vibrations. The absence of band around 1700 cm^{-1} is clearly indicative of the absence of carbonyl group of 2,6-diacetylpyridine. It is then assumed that carbonyl group was replaced by $>\text{C}=\text{N}$ when allowed to react with 1,3-diamino and 1,4-diaminobenzene for L_1 and L_2 cases.

TABLE-2
INFRARED SPECTRA (cm^{-1}) OF COMPLEXES OF Co(II) AND Ni(II) WITH LIGANDS L_1 and L_2

Complexes	$\nu(\text{C}=\text{N})$	$\delta(\text{--CH}_3)$	δ (-Pyridine)			$\nu(\text{C}\text{--}\text{H})$	
$[\text{Co}L_1]\text{Cl}_2$	1615	1350	1580	615	422	2910	2850
$[\text{Co}L_1](\text{NO}_3)_2$	1615	1355	1585	615	435	2915	2850
$[\text{Co}L_2]\text{Cl}_2$	1620	1350	1582	630	430	2920	2855
$[\text{Co}L_2](\text{NO}_3)_2$	1615	1360	1580	635	435	2924	2850
$[\text{Ni}L_1]\text{Cl}_2$	1620	1350	1585	640	422	2924	2855
$[\text{Ni}L_1](\text{NO}_3)_2$	1625	1360	1585	635	435	2924	2850
$[\text{Ni}L_2]\text{Cl}_2$	1620	1365	1580	640	430	2924	2856
$[\text{Ni}L_2](\text{NO}_3)_2$	1625	1365	1582	640	422	2920	2850

L_1 = bis(2,6-diacetylpyridine-1,3-diaminobenzene)

L_2 = bis(2,6-diacetylpyridine-1,4-diaminobenzene).

Magnetic susceptibilities of the compounds have been studied at room temperature using vibrating sample magnetometer from R.S.I.C., Madras. To determine the magnetic moment, the given data for a sample had least square fitted to a straight line and the slope was determined by plotting moment (EMU) values versus field strength (Kilogauss) at room temperature. Magnetic moments as well as visible spectra are given in Table-3.

Co(II) complexes of low spin type are found to possess moments in the range 1.95 to 2.15 B.M. Endicott *et al.*⁸ had also reported some Co(II) macrocyclic complexes in which μ_{eff} ranges from 1.1 B.M. to 2.22 B.M. Low spin Co(II) complexes are characterised^{9,10} by two ligand field bands located at 16000 and 20000 cm^{-1} . The present series of $[\text{ML}_1]\text{X}_2$, $[\text{ML}_2]\text{X}_2$ type complexes of Co(II) show bands around 17200 cm^{-1} and 20500 cm^{-1} which are assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ transitions respectively, indicating octahedral coordination around Co(II)¹¹⁻¹³.

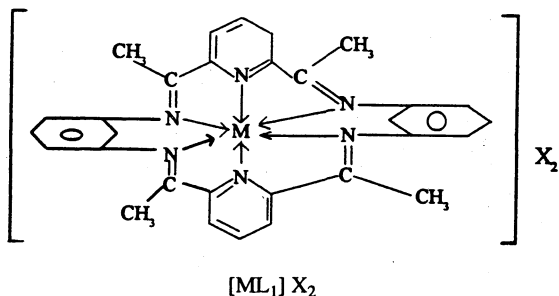
TABLE-3
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND MAGNETIC MOMENT VALUES

Complexes	Transitions, Absorption maxima (cm^{-1})				μ_{eff} (B.M.)
1. $[\text{CoL}_1]\text{Cl}_2$	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$ 17200		${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ 20500		1.95
2. $[\text{CoL}_1](\text{NO}_3)_2$	17300		20500		2.10
3. $[\text{CoL}_2]\text{Cl}_2$	17200		20400		2.15
4. $[\text{CoL}_2](\text{NO}_3)_2$	17200		20400		2.10
	${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$	${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g}$	${}^3\text{B}_{1g} \rightarrow {}^3\text{A}_{2g}$	${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_{2g}(\text{F})$	
5. $[\text{NiL}_1]\text{Cl}_2$	11200	12500	16850	23860	2.85
6. $[\text{NiL}_1](\text{NO}_3)_2$	11150	12800	17200	23800	2.90
7. $[\text{NiL}_2]\text{Cl}_2$	11250	12600	16980	25800	3.10
8. $[\text{NiL}_2](\text{NO}_3)_2$	11200	13000	17100	23800	3.15

L_1 = bis(2,6-diacetyl-pyridine-1,3-diaminobenzene),

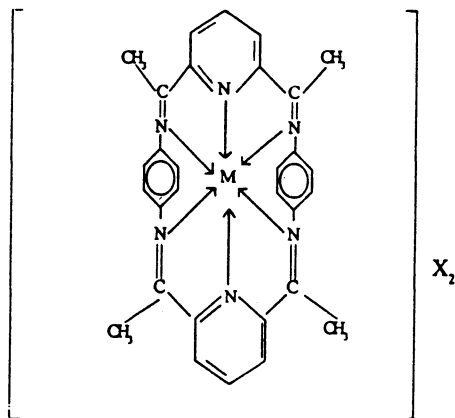
L_2 = bis(2,6-diacetyl-pyridine-1,4-diaminobenzene).

The nickel(II) macrocyclic complexes have magnetic moments ranging from 2.85 to 3.15 B.M. Complexes of $[\text{ML}_1]\text{X}_2$ and $[\text{ML}_2]\text{X}_2$ show two bands near 13000 cm^{-1} – 11200 cm^{-1} attributed to ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$ and ${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g}$ transitions respectively. In the high frequency region of the spectra bands observed at 17200 – 16850 and 25800 – 23860 cm^{-1} are assigned to the transitions ${}^3\text{B}_{1g} \rightarrow {}^3\text{A}_{2g}$ and ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g(\text{F})$ respectively. In spite of these bands, all the complexes show an intense band near 32800 cm^{-1} attributed to ${}^3\text{B}_{1g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ or ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$ transitions which seems to possess substantial charge transfer spectra. Based on chemical compositions and physico-chemical studies discussed above, distorted octahedral geometries have been proposed as shown in Figs. 1 and 2.



where $\text{M} = \text{Co(II)}, \text{Ni(II)}$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{NO}_3^-$ or OAc^-

Fig. 1



where M = Co(II), Ni(II), X = Cl⁻, Br⁻, NO₃⁻ or OAc⁻

Fig. 2

REFERENCES

1. M.G.B. Drew, A.H. Binothman, S.M. Nelson and P.D.A. Mcllory, *J. Chem. Soc., Dalton Trans.*, 2507 (1975).
2. R.D. Shannon and C.D. Prewitt, *Acta Cryst.*, 825, 925 (1969).
3. S.M. Nelson, S.G. McFall, M.G.B. Drew, A.H. Binothman and N.B. Meson, *J. Chem. Soc. Chem. Comm.*, 167 (1977).
4. F. Basolo and R.G. Pearson, *Mechanism of Inorganic. Reactions*, Wiley, New York, p. 146 (1968).
5. A. Braibanti, F. Dallavalle, M.A. Pellinghelli and E. Leporati, *Inorg. Chem.*, 7, 1430 (1968).
6. K. Nagano, H. Kinoshita and A. Hirakawa, *Chem. Pharm. Bull.*, 12, 1198 (1964).
7. D. Wester and G.J. Palenik, *Inorg. Chem.*, 15, 755 (1976).
8. J.F. Endicoff and B.S. Ramaswamy, *J. Am. Chem. Soc.*, 99, 429 (1977).
9. J. Chakroborty and B. Sahoo, *Indian J. Chem.*, 21A, 48 (1982).
10. J. Chakroborty and B. Sahoo, *Indian J. Chem.*, 21A, 441 (1982).
11. R.W. Mathews and R.A. Walton, *Inorg. Chem.*, 10, 1433 (1971).
12. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1968).
13. D.P. Rilleman, J.F. Endicoff and KaneMagne, *J. Chem. Soc. Chem. Comm.*, 495 (1972).
14. B.K. Mohapatra and B. Sahoo, *Indian J. Chem.*, 24A, 653 (1985).
15. J.G. Martin and Sue C. Cummings, *Inorg. Chem.*, 7, 1477 (1973).

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