

COBALT(III), NICKEL(II) AND ZINC(II) COMPLEXES WITH 4-(2-PYRIDYLAZO) RESORCINOL (PAR)

Mandalika S. Sastry, Ranjana Ghose and Animesh K. Ghose*

Department of Chemistry, Faculty of Science
Banaras Hindu University, Varanasi - 221005, India

(Received January 4, 1990; revised May 10, 1990)

ABSTRACT. Simple and mixed complexes of cobalt(III), nickel(II) and zinc(II) with 4-(2-pyridylazo)resorcinol (PAR) as one ligand and 1, 10-phenanthroline or 2,2'-bipyridyl as second ligand have been isolated and characterised by elemental analysis, conductivity, infrared, electronic spectra and room temperature magnetic measurements. The data suggest that the coordination of PAR occurs through its ortho-oxygen and pyridine nitrogen with a four coordinate geometry.

INTRODUCTION

The reagent 4-(2-pyridylazo)resorcinol (PAR), which is highly sensitive, has been used for the colorimetric determination of many metal ions (1). PAR, a water soluble azo dye, acts as a chelating agent in metal analysis and forms soluble chelates with a large number of metals (2). The literature survey reveals that the chelation of PAR involves the pyridine nitrogen, the *o*-hydroxyl group and azo nitrogen farthest from the heterocyclic ring (3). The chelation of metals by PAR is rapid and the stability constants are large. However, very little work has been reported on the solid complexes of PAR. Hence, it was deemed desirable, in the present study to investigate the chelating properties of PAR in absence and in presence of 1,10-phenanthroline (phen) or 2,2'-bipyridyl (bipy) with cobalt(II), nickel(II) and zinc(II) in the solid state.

MATERIALS AND METHODS

Synthesis. The simple complexes were prepared by refluxing a mixture containing sodium form of PAR (1 mmol) and metal nitrate (1 mmol) in ethyl alcohol for 16 hrs whereas, mixed ligand complexes containing PAR and phen or bipy were prepared by boiling under reflux, a mixture of the sodium salt of PAR (1 mmol), metal nitrate (1 mmol) and phen or bipy (1 mmol) for ~ 16 hrs. The precipitation of the complexes was done by concentrating the original solution to about one-third by heating and adding ethanol water mixture. The complexes were collected by filtration, washed several times with ethanol-water mixture, finally with ether and dried at ~ 50°C.

Analysis of the complexes. The metal ions in the complexes were determined by EDTA titration (4) after digesting the complexes in concentrated nitric acid. The carbon, hydrogen and nitrogen contents were analysed by Perkin-Elmer model 240 C elemental analyzer.

Physical measurements. IR spectra (as nujol mull for solid) measurements were made on a Perkin-Elmer 783 spectrophotometer in the region 4000-200 cm⁻¹. Solution electronic spectra of the complexes in ethanol were recorded using Perkin-Elmer Lambda-3 (200-900 nm) and Beckman model 5240 (900-1500

nm). Magnetic susceptibilities were determined by Faraday magnetic susceptibility balance at room temperature. Conductivity measurements were performed in ethanol by LBR/B type conductivity meter.

RESULTS AND DISCUSSION

All the complexes were coloured. The simple PAR complexes forms 1:2 stoichiometry (metal : ligand), whereas in mixed ligand complexes it is in 1:1:1 ratio (metal:PAR:phen or bipy), (Table 1). The synthesised complexes consist of complex cations and anions for all the complexes except for Ni(II) and Zn(II) 1:2 (metal : PAR) complexes. All the new complexes are soluble in common organic solvents. The melting points of all these compounds are greater than 300°C which indicate the contribution of the pyridine nitrogen to coordination by PAR (5). The conductance values at 10^{-3} molar concentrations indicate non-complex electrolyte of the 1:1 type. The low values observed are probably due to bulkiness of the cations, strong interaction in solution phase and ion-pair formation (6).

Table 1. Elemental analysis and some physical properties of the complexes.

Complex	Colour	Found (calc.) %				Molar conductance		Magnetic moment μ_B 298 K
		M	C	H	N	$\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$		
[Co(PAR) ₂]NO ₃	Brown	9.27 (9.33)	41.90 (41.81)	2.65 (2.53)	15.59 (15.52)	4.1	4.1	2.78
[Co(PAR)(phen)](NO ₃) ₂	Brown	9.24 (9.26)	43.33 (43.37)	2.50 (2.51)	13.15 (13.20)	18.0	18.0	3.04
[Co(PAR)(bipy)](NO ₃) ₂	Brown	9.86 (9.91)	42.49 (42.40)	2.75 (2.69)	14.20 (14.13)	8.2	8.2	3.13
Ni(PAR) ₂	Brownish black	10.23 (10.31)	46.46 (46.38)	2.73 (2.81)	14.80 (14.76)	1.9	1.9	4.35
[Ni(PAR)(phen)]NO ₃	Brownish black	10.30 (10.22)	48.16 (48.07)	2.81 (2.78)	14.60 (14.63)	3.6	3.6	3.47
[Ni(PAR)(phen)]NO ₃	Brownish black	11.12 (11.03)	47.41 (47.36)	3.11 (3.01)	15.84 (15.78)	9.0	9.0	3.50
Zn(PAR) ₂	Merun	11.34 (11.29)	45.72 (45.61)	2.85 (2.76)	14.65 (14.51)	2.9	2.9	Diamagnetic
[Zn(PAR)(phen)]NO ₃	Merun	11.17 (11.25)	47.60 (47.52)	2.71 (2.75)	14.40 (14.46)	4.5	4.5	Diamagnetic
[Zn(PAR)(bipy)]NO ₃	Merun	12.18 (12.13)	46.85 (46.77)	2.95 (2.97)	15.64 (15.59)	5.8	5.8	Diamagnetic

PAR = 4-(2-pyridylazo)resorcinol; phen = 1,10-phenanthroline; bipy = 2,2'-bipyridyl.

Infrared spectra. Infrared spectra of PAR, phen and bipy are cited in the literature (7-10). The characteristic bands of ligands and their simple and mixed complexes are given in Table 2. In the spectrum of free PAR, three medium bands appear at 1625, 1595, 1552 cm^{-1} and one weak band at 1570 cm^{-1} , due to C=C and C=N stretching modes, these bands show shifting on complexation. This indicates the linkage of metal ions with the pyridine nitrogen. The band due to N=N stretching mode (7) remains almost unchanged in all the metal complexes, i.e. the azo-group is not involved in coordination. Shifts are also observed for the band at 1324 cm^{-1} , that comprise C-O and C-N modes. The strong band at 1210 cm^{-1} due to δ C-O, δ C-N and δ C-H in the free PAR is shifted towards lower frequencies on complexation through ortho-oxygen group of PAR. However, the band at 1266 cm^{-1} due to ν C-OH remains unchanged in the IR spectra of all the complexes. The data meanwhile suggest that PAR binds through its pyridine nitrogen and ortho-hydroxyl group with metal ions.

Table 2. Characteristic infrared bands of the ligands and their metal complexes (cm^{-1}).

Ligands and complexes	$\nu\text{C}=\text{C}$	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{C}$ $\nu\text{C}-\text{N}$	$\nu\text{N}=\text{N}$	$\nu\text{C}-\text{O}$ $\nu\text{C}-\text{N}$	$\nu\text{C}-\text{O} $	$\delta\text{C}-\text{O}$ $\delta\text{C}-\text{N}$ $\delta\text{C}-\text{H}$	$\nu_{\text{as}}\text{C}-\text{C}$	$\nu\text{C}-\text{H}$ (Hetero-cycle)	$\nu\text{M}-\text{N}$	$\nu\text{M}-\text{O}$
PAR	1625m, 1595m	1570w 1552m	-	1370s	1324m	1266w	1210m	-	-	-	-
[Co(PAR) ₂]	1582m	1552w 1538m	-	1377s	1294m	1250m	1186m	-	-	300m 290m	276m
[Ni(PAR) ₂]	1582m	1552vw 1538m	-	1375s	1310m	1268w	1200m	-	-	264m	278m
[Zn(PAR) ₂]	1590m	1548m 1536m	-	1375s	1310m	1268m	1200m	-	-	268w	276m
phen	-	-	1512m 1490w	-	-	-	-	-	720	-	-
[Co(PAR)(phen)]	1585m	1550w 1537w	1500w 1478w	1374s	1335w	1275m	1245m	-	722s	300m	276m
[Ni(PAR)(phen)]	1615w 1585m	1550w 1536w	1500w	1375s	1312w	1270w	1245m	-	722m	264m	276m
[Zn(PAR)(phen)]	1612m 1602m	1575w 1565w	1537m	1375s	1334m	1272w	1252m	-	720m	265m	276m
bipy	-	-	1580s 1420m	-	-	-	-	-	956	-	-
[Co(PAR)(bipy)]	- 1585m	1552w 1526m	- 1408vw	1374s	1334w	1278w	1200m	997w	-	300m 290w	276m
[Ni(PAR)(bipy)]	- 1585m	1552w 1537w	- 1405vw	1374s	1312m	1270w	1200m	960w	-	264w	276w
[Zn(PAR)(bipy)]	1612m 1602m	1575w 1565w	1550m -	1375s	1334m	1270w	1250m	948m	-	268m	280m

PAR = 4-(2-pyridyl)azo(resorcinol); phen = 1,10-phenanthroline; bipy = 2,2'-bipyridyl.
The ring breathing frequency of phenanthroline was found at 1420 cm^{-1} (s).

The IR spectra of the mixed ligand complexes show shifting, in addition to the bands of PAR described above, in the frequencies of C-C and C-N stretching bands of phen ($1512, 1490\text{ cm}^{-1}$) and bipy ($1580, 1420\text{ cm}^{-1}$) (10) with respect of the free ligands. The data suggest that both nitrogen atoms of pyridine rings of phen and bipy are taking part in coordination with the metal ions.

The occurrence of medium intensity $\nu\text{M}-\text{O}$ bands at $276-280\text{ cm}^{-1}$ in the spectra of all the complexes favours coordination number four (11). The bands appearing at 290, 300 in cobalt(III), 264 in nickel(II) and 265, 268 cm^{-1} in zinc complexes may be attributed to $\nu\text{M}-\text{N}$ (12). The strong IR bands appearing in the ranges $1380-1310\text{ cm}^{-1}$ and $850-825\text{ cm}^{-1}$ (13), for simple and mixed complexes of Co(II) ion and mixed complexes of Ni(II) and Zn(II) ions, indicate the presence of nitrate in these complexes.

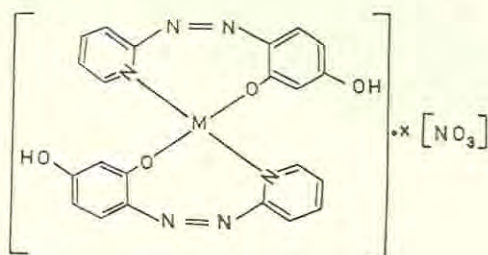
Electronic spectra and magnetic properties. PAR gave two electronic absorption bands in the presence of organic solvents, in UV and in visible regions, due to the excitation of π -electrons of both the phenyl ring and the azo group respectively (14). Also, the electronic absorption spectra of PAR in presence of both different pH's and metals, leads to bathochromic shift of the bands. This could be explained from the successive ionization of PAR and the easier excitation of the π -electrons of the azo chromophore.

The π -electron system of PAR (resorcinol) is small and is subjected to a flowing effect of electrons from the dissociated 1-hydroxyl group of PAR into the benzene ring. These effects would stabilize the trivalent state of cobalt in the PAR chelate. Thus, in solutions of cobalt-PAR chelates the cobalt(III) states could be stabilised even in the presence of reducing agent such as ascorbic acid (15). The solution electronic spectra of cobalt(II) compounds exhibit only one broad maximum band at about 515 nm (7). The electronic spectra of nickel(II)

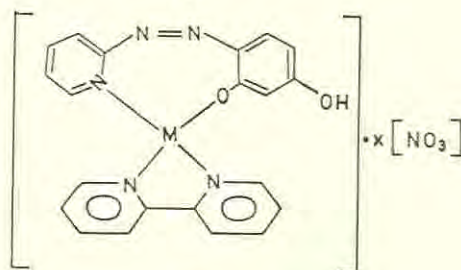
complexes exhibit bands with λ_{\max} 440, 540, 1160 nm suggesting four coordinated geometry (16). The first two bands may also be ascribed to those of $\pi-\pi^*$ transition due to the coordination of O-hydroxyl group (17).

The magnetic moments of cobalt(III) complexes are 2.78, 3.04 and 3.13 μ_B for Co(III)-PAR, Co(III)-PAR-bipy complexes. The data correspond to dsp^2 hybridization, and the simple as well as the mixed ligand complexes of PAR with cobalt(III) have four coordinated geometry (18). The magnetic moments of the nickel(II) compounds are 4.35, 3.47 and 3.50 μ_B for Ni(II)-PAR, Ni(II)-PAR-phen and Ni(II)-PAR-bipy respectively, suggesting tetrahedral structures (19).

On the basis of the above studies the following tentative structures (I and II) for simple and mixed ligand complexes, are proposed. The presence of 8-membered ring chelates are not very uncommon (18). To economise the space one representative structure of mixed complexes with bipy, is given.



(I)



(II)

M = Co(III), Ni(II) or Zn(II)

X = 1 for Co(III) and x = 0 for Zn(II) and Ni(II) simple complexes with PAR

x = 2 for Co(III) and x = 1 for Ni(II) and Zn(II) in mixed ligand complexes.

ACKNOWLEDGEMENT

Authors are thankful for the financial help from the U.G.C., New Delhi for granting fellowship to M.S.S. and Research Associateship to R.G.

REFERENCES

1. S. Shibata in A.J. Baranard and H. Flaschka (Eds), "Chelates in Analytical Chemistry", M. Dekker, New York, Vol. 3, 132 (1972).

2. E.B. Sandell and H. Onishi, "Photometric Determination of Traces of Metals", Wiley, New York, 1978.
3. R.G. Anderson and G. Nickless, *Analyst.*, **92**, 207 (1967).
4. H.A. Flaschka, "EDTA Titrations" Pergamon, London, 1964.
5. W.J. Geary, G. Nickless and F.H. Pollard, *Anal. Chim. Acta*, **27**, 71 (1962).
6. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
7. M. Siroki, L.J. Maric, Z. Stefanac and M.J. Herak, *Inorg. Chim. Acta*, **75**, 101 (1975).
8. M. Siroki and C. Djordjevic, *J. Less Common Metals*, **23**, 228 (1971).
9. M.V. Krishna Murthy, I.M. Rao and D. Satyanarayana, *Indian J. Chem.*, **21A**, 827 (1982).
10. M.S. Sastry, R. Ghose and A.K. Ghose, *Transition Met. Chem.*, **13**, 447 (1988).
11. M. Goodgame and K.W. Johns, *J. Chem. Soc. Dalton*, 1294 (1978).
12. C.M. Mikulski, F.J. Iaconianni, L.L. Pytlewski, A.N. Speca and N.M. Karayannis, *Inorg. Chim. Acta*, **46**, L47, (1980) and refs. therein.
13. N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).
14. J.P. Hart and W.F. Smith, *Spectrochim. Acta*, **36A**, 279 (1980).
15. T. Iwamoto and M. Fujimoto, *Anal. Chim. Acta*, **29**, 282 (1963).
16. A.B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
17. Y. Kudo, N. Yoshida and M. Fujimoto, *Bull. Chem. Soc. Jpn.* **59**, 795 (1986).
18. A.E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice Hall, New York, 1956.
19. B.N. Figgis and J. Lewis, "Progress in Inorganic Chemistry", Interscience Publications, New York, Vol. **6**, 207 (1964).