© *Proc. Indian natn. Sci. Acad.*, **49**, A, No. 1. 1983, pp. 118-123.
Printed in India.

Analytical Chemistry

COPPER(II), COBALT(III) AND IRON(II) COMPLEXES OF PYRIDYLHYDRAZONE OF SALICYLALDEHYDE (PHSAL)

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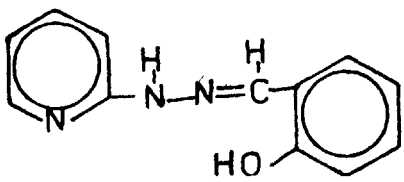
(*Received 19 January 1982; after revision 17 January 1983*)

Octahedral copper(II), cobalt(III) and Iron(II) complexes of pyridylhydrazone of salicylaldehyde have been synthesised. ESR spectra of the copper(II) complexes have been recorded in polycrystalline state, in DMF and DMSO solution at RT and in chloroform solution at LNT (in frozen state). The spectra are characterstic of octahedral geometry with $d_{x^2-y^2}$ as ground state. $^5T_{2g}$ ground state has been inferred from the temperature independent magnetic moment (5.20 $\pm$ 0.05 BM) for the iron complex in the temperature range 300–80°K.

Keywords : Copper(II); Iron(II); Cobalt(III); Pyridylhydrazone of Salicylaldehyde; Octahedral Geometry

INTRODUCTION

TRIDENTATE heterocyclic hydrazones have been recently used as potential analytical reagents in the micro determination of various metal ions (Shibata, 1972). It is only recently that the transition metal complexes of this important class of compounds have been synthesized and studied by various physico-chemical techniques (Bhoon & Majer, 1977; Bhoon *et al.*, 1976; 1979; Betteridge & John, 1968; and Chiswell *et al.*, 1964). The present communication describes the synthesis of copper(II), iron(II) and cobalt(III) complexes of pyridylhydrazone of salicylaldehyde, I(PHSAL-H) and their characterization by magnetic measurements, absorption and ESR spectral studies. Octahedral geometry is assigned to all the complexes.



PHSAL—H, I

EXPERIMENTAL

Preparation of PHSAL—H

The ligand was synthesized by the condensation of 2-hydrazinopyridine and salicylaldehyde in slightly acidic medium which resulted in the immediate

precipitation of a white crystalline compound which was recrystallized from chloroform. PHSAL-H requires C = 69.33 per cent, N = 18.66 per cent and H = 4.88 per cent and was found to have C = 69.05 per cent, N = 18.43 per cent and H = 4.78 per cent.

Preparation of Complexes

(*i*) *Preparation of Copper(II) Complexes* : Aqueous solution of the appropriate copper(II) salts was added to the aqueous alcoholic solution of PHSAL-H in equimolar ratio and the resulting solution was refluxed for two hours on a water bath. Green coloured compounds separated out in each case on concentrating the solution which were filtered off, washed successively with acetone and ether and dried in a vacuum desiccator over silica-gel.

(*ii*) Nickel(II), cobalt(III) and iron(II) complexes were also prepared in the same way.

Physical Measurements

Magnetic susceptibility measurements in powdered state at room temperature were carried out on a Gouy balance using Hg [Co(CNS)$_4$] as the calibrant. However,

TABLE I

Micro analysis and magnetic moment data for the complexes

Compound	%M Calcd. (found)	%C Calcd. (found)	%N Calcd. (found)	%H Calcd. (found)	Temp. (OK)	μeff (B.M)
[Cu^{II}(PHSAL)Cl.2H_2O]	16.85	41.37	11.14	4.24		
	(16.67)	(41.21)	(11.04)	(4.14)	300	1.98
[Cu^{II}(PHSAL)OAc.2H_2O]	17.43	49.37	11.32	4.11		
	(17.38)	(49.21)	(11.28)	(4.03)	300	1.87
[Cu^{II}(PHSAL)SO_4.2H_2O]	16.56	41.98	11.30	3.77		
	(16.43)	(41.84)	(11.24)	(3.65)	300	1.85
[Co^{III}(PHSAL)$_2$Cl]	10.82	57.32	15.42	3.67		
	(10.67)	(57.21)	(15.31)	(3.55)	300	—
[Fe^{II}(PHSAL)C]	11.04	61.67	16.60	3.95		
	(10.08)	(61.64)	(16.48)	(3.84)	298	5.26
					256.5	5.22
					222.0	5.22
					206.0	5.18
					186.0	5.17
					169.5	5.15
					157.5	5.23
					137.0	5.26
					124.5	5.23
					110.0	5.25
					91.5	5.24

the susceptibility measurements at different temperature on [Fe(PHSAL)$_2$] were carried out on a Faraday assembly fitted with an electrobalance which displaced directly the pull in mg. The ESR spectra were recorded on a E-4 Varian ESR spectrometer. The electronic spectra were recorded in nujol mull on DMR-21 UV-Visible-IR spectrophotometer. The complexes were analyzed for C, H and N contents in the Micro-Analytical Laboratory; CIBA-GEIGY-Research Centre, Goregaon, Bombay and metal contents were determined by atomic absorption.

Results and Discussion

The results of elemental analysis and magnetic susceptibility measurements on the complexes are presented in Table I. The magnetic moment values for the copper(II) complexes are in the range 1.83–2.00BM which corrosponds to the magnitude expected (Figgis & Harris, 1959; and Fritz *et al.*, 1958) for normal octahedral copper(II) complexes. The absorption spectra of the complexes recorded as mull show a well defined band centred in the range 16000–17550cm^{-1} which could be assignable to $t_{2g} \longrightarrow e_g$. The octahedral geometry in the copper(II) complexes is

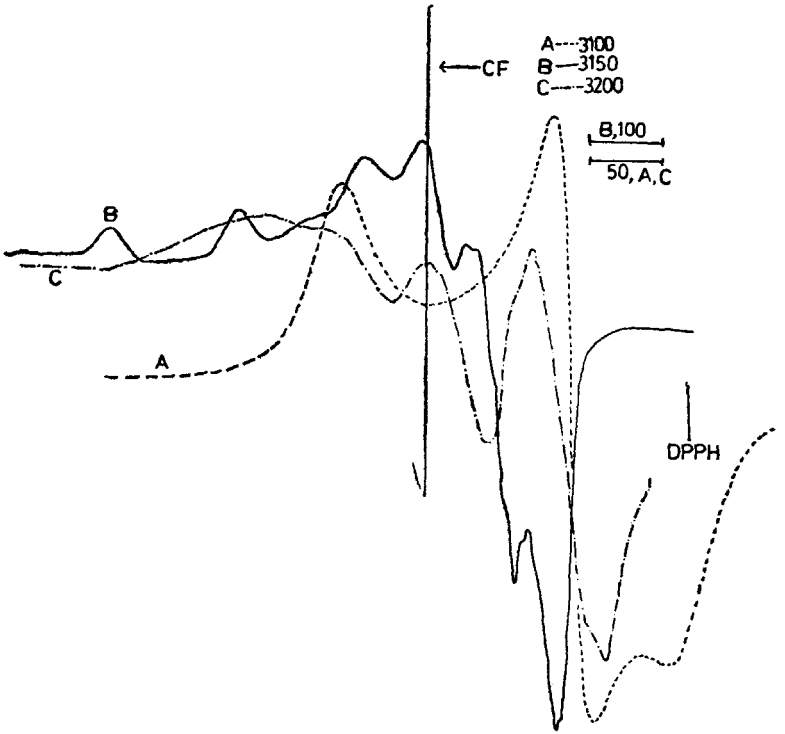


Fig. 1 ESR spectra of complexes

A. [Cu^{II}(PHSAL). Cl.2H$_2$O], RT Powder,

B. [Cu^{II}(PHSAL). ½SO$_4$.2H$_2$O], Frozen soln,

C. [Cu^{II}(PHSAL). ½SO$_4$.2H$_2$O], RT. DMF soln.

further confirmed by the ESR spectra of the complexes in frozen chloroform solution which is characterstic of octahedral copper(II) complexes with $d_{x^2-y^2}$ as the ground state. The terdentate character of PHSAL-H, coordinating through the heterocyclic nitrogen, nitrogen of the azo group farther from heterocyclic ring and the oxygen of the phenolic group is confirmed by the splitting of the $g_\perp$ in the ESR spectra in frozen state showing five lines. Some of the ESR parameters calculated from the frozen solution, polycrystalline and DMF/DMSO solution spectra (Figs. 1, 2) are presented in Table II.

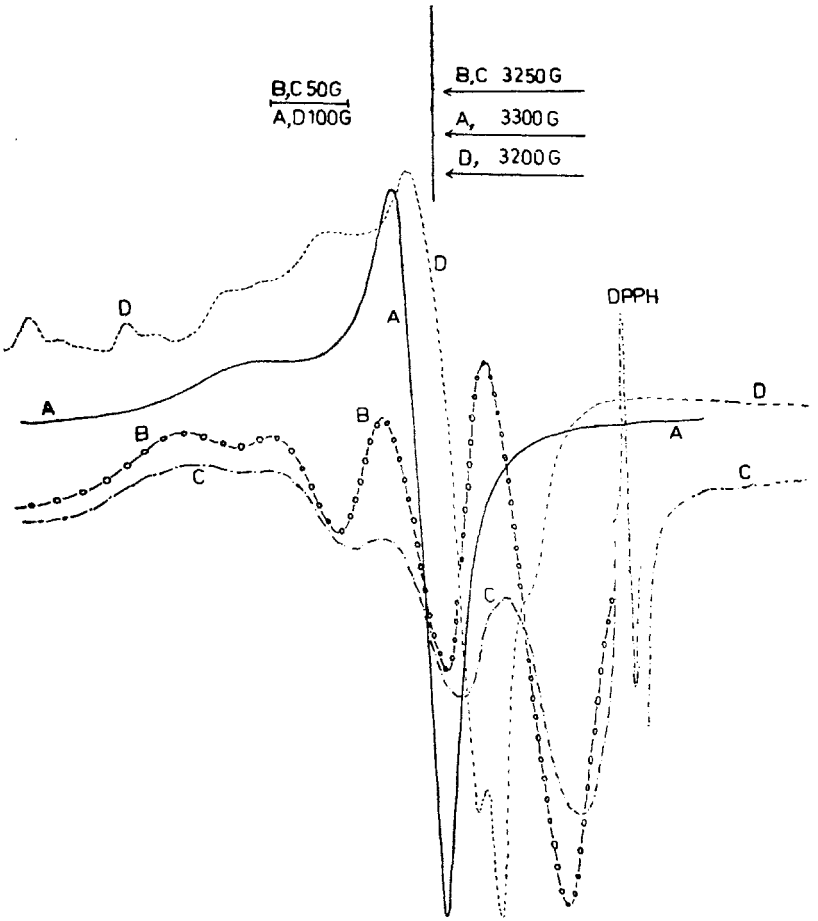


FIG. 2. ESR spectra of complexes

A. [Cu^{II}(PHSAL) 1/2 SO_4.2H_2O], RT, Powder

B. [Cu^{II}(PHSAL) Cl.2H_2O], RT, DMF soln.

C. [Cu^{II}(PHSAL) (OAc)2H_2O], RT, DMF soln.

D. [Cu^{II}(PHSAL) Cl.2H_2O], Frozen soln.

TABLE II

ESR parameters for copper(II) complexes

Compound	Temp.	$g_\perp$ $g_{\|\|}$	g_z $g_\perp$	g_3	$\langle g \rangle = \frac{1}{3}(g_{\|\|}+2g_\perp)$	A^{Cu}	AN
$[Cu^{II}(PHSAL)Cl.2H_2O]H_2O$	Polycrystalline (RT)	2.195	2.085	2.044			
	$CHCl_3$, LNT	2.205	2.068		2.114	135G	30G
	DMF, RT				2.119		
$[Cu^{II}(PHSAL)SO_4.2H_2O]$	Polycrystalline (RT)	2.269	2.103				
	$CHCl_3$,LNT	2.231	2.050		2.110	175G	20G
	DMF, RT				2.142		15G
$[Cu^{II}(PHSAL)(CH_3CO^dO)2H_2O]$	Polycrystalline (RT)	2.225	2.013				
	$CHCl_3$, LNT				2.123		
	DMF, RT						

Cobalt complex is diamagnetic and hence it is assigned octahedral structure, the change of oxidation state is obviously due to oxidation.

The magnetic moment of the iron(II) complex is found to be 5.26BM at room temperature and the magnetic moment is also temperature independent in the temperature range 300–80°K. $^5T_{2g}$ ground state (Bose & Rai, 1965; and Gill, 1961) in iron(II) octahedral complex is concluded from this behaviour.

ACKNOWLEDGEMENT

The author is thankful to Dr S. Mitra, Chemical Physics Group, TIFR, Bombay for permitting to carry out the variable susceptibility measurements. The Director, CIBA–Geigy Research Centre Goregaon, Bombay for the Micro-Analysis. The ESR spectral studies were carried out as National Associate in RSIC, I.I.T., Madras and the author is thankful to Head, RSIC, I.I.T, Madras for permitting to use the instrumental facilities.

REFERENCES

Betteridge, D., and John, D. (1968) Mass spectra of some bivalent transition-metal ion chelates with pyridylazo phenols and naphthols. *Talanta*, **15**, 1227.

Bhoon, Y. K., and Majer, J. R. (1977) Mass Spectral studies on 1-(2-pyridylazo)-2-phenanthrol and its metal chelates. *Indian J. Chem.* **15A**, 1019.

Bhoon, Y. K., Pandeya, K. B., and Singh, R. P. (1976) Magnetic exchange interactions and Spin-state equilibrium in cobalt(II) chelates of 1-(2-pyridylazo)-2-phenanthrol (PAPL). *J. Coord. Chem.*, **6**, 71.

Bhoon, Y. K., Singh, R. P., and Gregson, A. K. (1979) Ferromagnetic interactions in a Cobalt(II) complex of PAPL. *J. Coord. Chem.*, **9**, 251.

Bose, A., and Rai, R. (1965) Ligand field theory of susceptibility and anisotropy in trigonally distorted Fe^{3+} complexes. *Indian. J. Phys.* **38**, 176.

Chiswell, B., Lions, F., and Tomlinson, M. L. (1964) Tridentate chelate compounds IV. Metal complexes from α-Diketonone mono-α- pyridylhydrazone type ligands. *Inorg. Chem.*, **3**, 492.

Figgis, B. N., and Harris, C. M. (1959) Magnetochemistry Part III. Compounds of bivalent copper. *J. chem. Soc.*, 855.

Fritz, J. J., Rao, R. V. G., and Seki, S. (1958) Magnetic susceptibility at low temperature of 'complex' inorganic salts of the first transition group. *J. phys. Chem.*, **62**, 703.

Gill, S. N. (1961) Complex halides of the transition metals Part II. Tetrahedral iron complexes. *J. chem. Soc.*, 3512.

Shibata, S. (1972) Metal complexes of 2-pyridylazo compounds. In : *Chelates in Analytical Chemistry*. (Eds. : H. A. Flashka and A. U. Bernard) Marcell Dekker, New York, 1.