

## Synthesis and spectral studies of metal complexes of (3,4-dihydro-3-oxo-2H-1,4-benzoxazin-2-yl) acetic acid hydrazones of benzaldehyde, salicylaldehyde and furfuraldehyde

Ch. THIRUPATAIAH, D. PRABHAKARA CHARY<sup>1</sup> M. RAVINDER and S. SRIHARI\*

Department of Chemistry, Kakatiya University, Warangal - 506 009 (India).

<sup>#</sup>Department of Physical Sciences, KITS, Warangal (India).

(Received: October 11, 2008; Accepted: November 24, 2008)

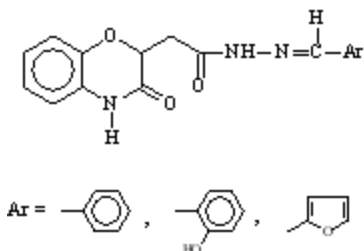
### ABSTRACT

Several new metal complexes of Fe(III), Ni(II), Zn(II), Ru(III) and Pd(II) with hydrazones derived from (3,4-dihydro-3-oxo-2H-1,4-benzoxazin-2-yl)acetic acid hydrazide and benzaldehyde, salicylaldehyde and furfuraldehyde and reported. The ligands co-ordinate with the metal ions in neutral, bidentate / mononegative, tridentate manner. The Fe(III), Ni(II) and Ru(III) complexes are found to be octahedral, Pd(II) complexes square planar and the Zn(II) complexes tetrahedral.

**Key words :** Metal complexes of aldacid hydrazones-structural studies.

### INTRODUCTION

Hydrazones constitute an important class of organic compounds owing to their co-ordinating capability<sup>1</sup>, analytical and industrial potentiality<sup>2,3</sup>, and biological activity<sup>4,5</sup>. In view of the importance associated with this class of compounds, a study has been undertaken and the present paper describes the preparation and structural characterization of Fe(III), Ni(II), Zn(II), Ru(III) and Pd(II) complexes of (3,4-dihydro-3-oxo-2H-1,4-benzoxazin-2-yl)acetic acid hydrazones of benzaldehyde, salicylaldehyde and furfuraldehyde abbreviated respectively as BBAH, SBAH and FBAH.



### EXPERIMENTAL

The ligands BBAH, SBAH and FBAH were prepared as reported earlier<sup>6,7</sup>. The Fe(III), Ru(III), Pd(II), Ni(II) and Zn(II) complexes of the ligands were prepared taking respective metal chlorides in the first three, and acetates in the last two in 1:2 (metal : ligand) molar ratio using required quantities of aqueous methanol or methanol. So as to effect the solubility of the metal salts and the ligands and refluxing the mixture on a hot water bath for about 3 hrs. The solids that separated out were filtered, washed with water, methanol and ether and were dried in vacuum over fused CaCl<sub>2</sub>.

The C, H and N analysis of the complexes was done at RSIC, CDRI, Lucknow. Metal contents were determined using standard methods. The molar conductivity measurements of the complexes in DMF at 10<sup>-3</sup> M concentration were made on a Digisign digital conductivity meter DI 909 model. Gouy balance calibrated with Hg[CO(NCS)<sub>4</sub>] was used to measure the magnetic susceptibility of the

complexes in solid state at room temperature. The thermogravimetric curves of the complexes were recorded with a Mettler TA 3000 system. The IR spectra of the ligands and the complexes in KBr or in Nujol mulls in the range 4000-200  $\text{cm}^{-1}$  were recorded using IR spectrophotometer acculab 10 and also Perkin Elmer Model-283 IR spectrophotometer. The electronic spectra of the complexes in DMF was obtained employing Shimadzu UV-vis spectrophotometer UV-160 A. The Mossbauer spectra of Fe(III) complexes against Fe-foil were procured from the Department of Nuclear Physics, University of Madras, Chennai. The Varian E-4 X-band spectrophotometer operating in the frequency range 8.8 – 9.6 GHz was employed in recording ESR spectra of Ru(III) complexes in solid state at room temperature and in DMF solution at LNT.

## RESULTS AND DISCUSSION

All the metal complexes (Table 1) are coloured, non hygroscopic and stable in air, at room temperature. They are insoluble in water and simple

organic solvents but soluble in DMF and DMSO. The molar conductance data suggest that the Fe(III) and Ru(III) complexes are 1:1 electrolytes while the Ni(II), Zn(II) and Pd(II) complexes are nonelectrolytes<sup>8</sup>. The magnetic moment data indicate that the Fe(III), Ru(III) and Ni(II) complexes are paramagnetic corresponding respectively to five. One and two unpaired electrons and that the Zn(II) and Pd(II) complexes are diamagnetic.

The thermal behaviour of the Fe(III), Ni(II), Zn(II), Ru(III) and Pd(II) complexes formed of SBAH reveals different initial decomposition temperatures (Fe-SBAH = 220°; Ni-SBAH = 270°; Zn-SBAH = 190°; Ru-SBAH = 230° and Pd-SBAH = 210°) and the final product of decomposition corresponds in each case, to metal oxide. Taking the initial decomposition temperatures of the complexes as a measure of their thermal stability, the stability order of the complexes may be computed as Ni > Ru > Fe > Pd > Zn.

All the ligands show small or medium intensity band around 3400 and 3200  $\text{cm}^{-1}$ . The

**Table 1: Analytical and physical data of the complexes**

Complex	Colour	Metal % Found (calc)	Molar Cond. ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMF)	$\mu_{\text{eff}}$ (BM)
[Fe(BBAH) <sub>2</sub> Cl <sub>2</sub> ]Cl	Black	6.96 (7.15)	69	5.73
[Ni(BBAH) <sub>2</sub> (OAc) <sub>2</sub> ]	Red	7.21(7.38)	15	3.03
[Zn(BBAH) <sub>2</sub> (OAc) <sub>2</sub> ]	Yellow	13.03(13.26)	14	Dia
*[Ru(BBAH) <sub>2</sub> Cl <sub>2</sub> ]Cl	Blue	-	75	1.92
[Pd(BBAH) <sub>2</sub> Cl <sub>2</sub> ]	Orange	21.63(21.86)	12	Dia
[Fe(SBAH-H) <sub>2</sub> ]Cl	Brown	7.29(7.55)	63	5.45
[Ni(SBAH-H) <sub>2</sub> ]	Maroon	8.11(8.30)	17	2.95
[Zn(SBAH-H)(OAc)]	Yellow	14.32(14.56)	16	Dia
*[Ru(SBAH-H) <sub>2</sub> ]Cl	Brown	-	65	1.93
[Fe(FBAH) <sub>2</sub> Cl <sub>2</sub> ]Cl	Black	7.19(7.34)	77	5.82
[Ni(FBAH) <sub>2</sub> (OAc) <sub>2</sub> ]	Brown	7.89(7.57)	16	3.09
[Zn(FBAH) <sub>2</sub> (OAc) <sub>2</sub> ]	Yellow	13.41(13.54)	14	Dia
*[Ru(FBAH) <sub>2</sub> Cl <sub>2</sub> ]Cl	Blue	-	74	1.92
[Pd(FBAH)Cl <sub>2</sub> ]	Orange	2	15	Dia

All the compounds gave satisfactory C, H and N analyses

\*Ru content not determined.

former of which has been assigned to free NH stretching<sup>9</sup> and the latter to ring NH stretching involved in hydrogen bonding with lactam carbonyl<sup>10</sup>. A strong band at 1670 cm<sup>-1</sup> in all the ligands is attributed to  $\nu$ C=O or ring amide<sup>11</sup>. The antisymmetric stretching frequency corresponding to C-O-C group in the ligands has been observed at 1120 cm<sup>-1</sup>. All these bands remain unaltered in the spectra of the metal complexes ruling out the possibility of enolization of the involvement of nitrogen and oxygen of these groups in coordination. All the ligands display a medium intensity band around 1580 cm<sup>-1</sup> to  $\nu$ C=O of aliphatic amide<sup>12</sup>. This band undergoes a lower shift by about 100 cm<sup>-1</sup> indicating that the oxygen of this group is involved in bonding with the metal ions. Another medium or small intensity band that makes its presence in all the ligands around 1610 cm<sup>-1</sup> due to

$\nu$ C=N has been found lower shifted by 20-40 cm<sup>-1</sup> in the complexes. The downward shift of this frequency in the complexes suggests that the nitrogen of this group is in co-ordination with the metal ions<sup>13</sup>. The ligand SBAH records somewhat a broad band at 3040 cm<sup>-1</sup> ascribable to  $\nu$ O-H associated through intermolecular hydrogen bonding. This band disappears in the spectra of its complexes indicating that the diprotonation of the group as taken place. A medium intensity band at 1240 cm<sup>-1</sup> in this ligand assignable to  $\nu$ C-O is seen to have undergone a positive shift by 50 cm<sup>-1</sup> in its complexes. This positive shift which indicates coordination of the deprotonated hydroxy group may be attributed to the drift of electron density from oxygen to the metal ions resulting in greater ionic character of the  $\nu$ C-O bond and a consequent increase in  $\nu$ C-O vibration frequency<sup>14</sup>. The co-

**Table 2: Electronic spectral data of the metal complexes**

Metal complex	Frequency (cm <sup>-1</sup> )			B (cm <sup>-1</sup> )	C (cm <sup>-1</sup> )	10Dq (cm <sup>-1</sup> )	$\beta$
Fe-BBAH	16000	19230	24510	-	-	-	-
Ni-BBAH	9300	14820	25000	795	-	9300	0.772
Zn-BBAH	>30000 cm <sup>-1</sup> charge transfer spectra						
Ru-BBAH	14925	18870	24630	493	1972	25278	0.78
Pd-BBAH	14290	16670	25640	-	-	-	-
Fe-SBAH	15060	17860	23260	-	-	-	-
Ni-SBAH	9520	14925	24270	709	-	9520	0.688
Zn-SBAH	>30000 cm <sup>-1</sup> charge transfer spectra						
Ru-SBAH	14490	18520	24690	504	2016	25073	0.80
Pd-SBAH	14090	16130	23260	-	-	-	-
Fe-FBAH	16810	19610	23810	-	-	-	-
Ni-FBAH	9260	14490	25640	823	-	9260	0.799
Zn-FBAH	>30000 cm <sup>-1</sup> charge transfer spectra						
Ru-FBAH	14290	17860	24390	446	1784	23657	0.71
Pd-FBAH	14490	15870	25000	-	-	-	-

**Table 3**

Complex	$g_{\perp}$	$g_{\parallel}$	$g_{av}$	$A_{\perp}$ (G)	$A_{\parallel}$ (G)	$A_{ave}$ (G)
Ru-BBAH	2.33	1.95	2.20	138	83	120
Ru-SBAH	2.13	1.96	2.07	55	70	60
Ru-FBAH	2.14	1.99	2.09	70	50	63

ordination through oxygen of aliphatic amide group and nitrogen of azomethine group in all the ligands and additionally through oxygen of phenolic C-O group in SBAH is further substantiated by the appearance in all the complexes of non-ligand bands in the far infrared region around 500 and 400  $\text{cm}^{-1}$  assignable to  $\nu\text{M-O}$  and  $\nu\text{M-N}$  respectively<sup>15</sup>. In addition, Fe and Ru complexes of BBAH and FBAH and Pd complexes of all the three ligands show a band around 300  $\text{cm}^{-1}$  assignable to  $\nu\text{M-Cl}$ <sup>16</sup> and the Zn complexes of all the three ligands and Ni complexes of BBAH and FBAH display medium or low intensity bands around 1550, 1420 and 1310  $\text{cm}^{-1}$  which may be assigned respectively to  $\nu(\text{COO})$ ,  $\nu(\text{COO})$  and  $\nu\text{CH}_3$  vibrations of the coordinated acetate present in them<sup>17</sup>.

The electronic spectral frequencies observed for the complexes along with ligand field parameters for the Ru(III), Ni(II) complexes are given in Table 2. These frequencies may be assigned, in the increasing order, to the transitions as detailed below.

Fe(III) complexes :  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$ ,  
 Ni(II) complexes :  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$   
 Ru(III) complexes :  ${}^2\text{T}_{2g} \rightarrow {}^4\text{T}_{1g}$ ,  ${}^2\text{T}_{2g} \rightarrow {}^4\text{T}_{2g}$  and  ${}^2\text{T}_{2g} \rightarrow {}^2\text{A}_{2g}$   
 Pd(II) complexes :  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ ,  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$

Based on these transitions and the other data observed, high-spin octahedral geometry<sup>18</sup> for the Fe(III) complexes, octahedral geometry<sup>19</sup> for the Ni(II) complexes, low spin octahedral<sup>19</sup> geometry for Ru(III) complexes and square planar geometry for Pd(II) complexes have been proposed.

The Zn(II) complexes show no d-d bands as is the case with a  $d^{10}$  system and based on the other data obtained, tetrahedral geometry has been proposed for them.

The ligand field parameters 10 Dq, B and C have been calculated for the Ru(III) complexes using the transitions<sup>20</sup>.

$$\begin{aligned} {}^2\text{T}_{2g} \rightarrow {}^4\text{T}_{1g} &= 10\text{DQ} - 5\text{B} - 4\text{C} \\ {}^2\text{T}_{2g} \rightarrow {}^4\text{T}_{2g} &= 10\text{DQ} + 3\text{B} - 4\text{C} \end{aligned}$$

and assuming that  $\text{C/B} = 4$ .

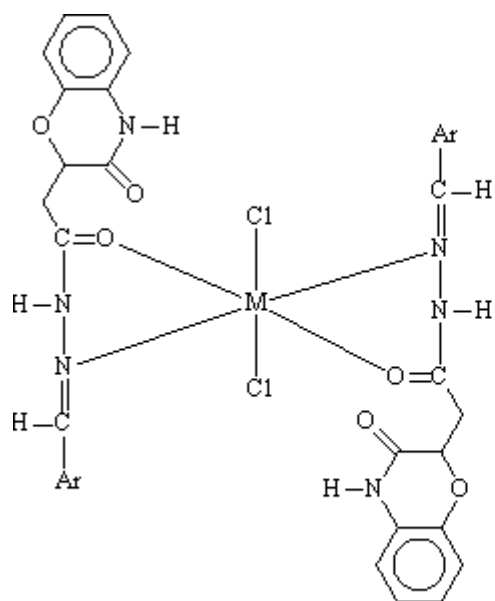
The Racah interelectron repulsion parameter B observed for the complexes is less than that for the Ru(III) ion ( $\text{B}' = 630\text{ cm}^{-1}$ )<sup>21</sup>. 10 DQ value is high and further, the nephelauxetic parameter  $\beta = \text{B/B}'$  is less than one. All these observations suggest that the metal-ligand bond in the present complexes is covalent in nature<sup>22</sup>. The Racah inter-electronic repulsion parameter (B) and nephelauxetic parameter ( $\beta$ ) for Ni(II) complexes ( $\text{B} = 709\text{-}823\text{ cm}^{-1}$   $\beta = 0.69 - 0.80$ ) suggest considerable amount of covalent character of the metal ligand bond in them<sup>23-25</sup>.

The ESR spectral data for the Ru(III) complexes are incorporated in Table 3.

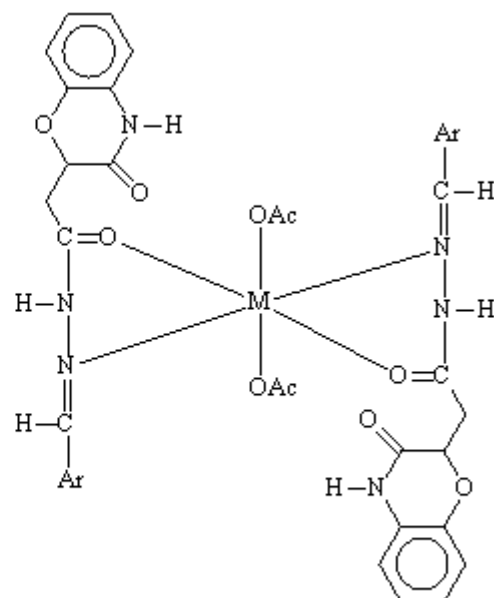
The spectra of Ru(III) complexes in solid state at room temperature are anisotropic and each show two peaks, one sharp peak of large intensity to the left of DPPH and the other broad peak of small intensity to the right of DPPH. The shape of these spectra may be rationalized in terms of the low spin nature of the complexes<sup>26</sup>. The solution spectra of the complexes at LNT are further resolved and show a six line pattern due to hyperfine interaction of the unpaired electron with the nuclear spin  $I_{\text{Ru}} = 5/2$  of Ru (Fig. 2). The ESR parameters calculated for the complexes from their solution spectra are presented in table 3 are as in good agreement with value in literature for the low spin Ru(III) octahedral complexes<sup>27</sup>.

The  $t_{2g}^5$  configuration of a Ru(III) complex constitutes a positive hole in  $t_{2g}$  orbital set and so  $g_{\perp} > g_{\parallel}$  is expected.

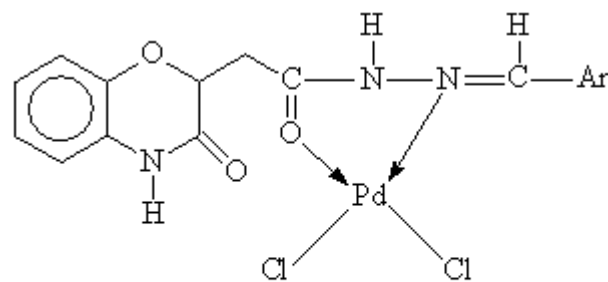
Based on the foregoing discussion, tentative structures for the representative metal complexes of BBAH may be proposed as follows.



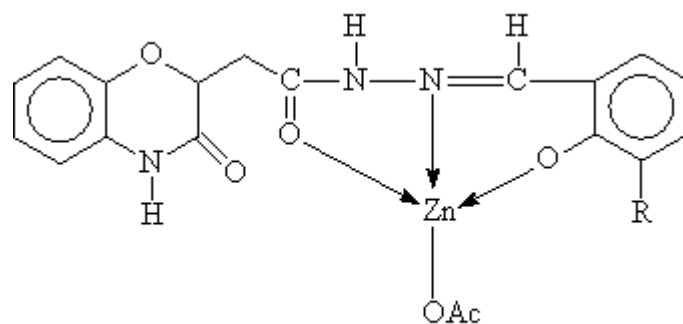
M = Fe, Ru



M = Ni



Square planar



Tetrahedral

## REFERENCES

1. R.L. Dutta and M.M. Hussain *J. Scient. Ind. Res.*, **44**: 635 (1985).
2. M. Katyal and Y. Dutt. *Talanta*, **22**: 151 (1975).
3. Yu, P. Kitaev, B.T. Buzykin and T.V. Troepol's Kaya, *Russ. Chem. Rev.*, **39**: 441 (1970).
4. T.S. Ma and T.M. Tien, *Antibiotics and Chemotherapy*, **3**: 491(1953).
5. R.S. Verma and W.L. Nobles, *J. Pharm. Sci.*, **64**: 881 (1975).
6. Y. Jayamma, A. Malla Reddy and V. Malla Reddy, *Indian Drugs*, **27**: 172 (1989).
7. D.R. Shridhar, Bhagat Ram, K. Srinivasa Rao and M.L. Jain, *Indian J. Chem.*, **24B**: 992 (1985).
8. W.J. Geary, *Coord. Chem. Rev.*, **7**: 81 (1971).
9. R.S. Drago, Physical methods in inorganic chemistry, Affiliated East-West Press Pvt. Ltd., New Delhi, 219 (1968).
10. V. Atre, V. Jaya Tyaga Raju, K. Jeeva Ratnam and M.C. Ganorkar, *Indian J. Chem.*, **23A**: 691 (1984).
11. Y. Jayamma, A. Malla Reddy and V. Malla Reddy, *Indian Drugs*, **27**: 172 (1989).
12. T.R. Rao, M. Sahay and R.C. Aggarwal, *Indian J. Chem.*, **23A**: 214 (1984).
13. R.L. Dutta and A.K. Sarkar, *J. Inorg. Nucl. Chem.*, **43**: 57 (1981).
14. D.V. Khanolkar and D.D. Khanolkar, *Indian J. Chem.*, **18A**: 315 (1979).
15. A. Syamal and M.R. Maurya, *Indian J. Chem.*, **24A**: 836 (1985).
16. R.J.H. Clark, *J. Chem. Soc.*, 1377 (1963).
17. K. Nakamoto, Infrared and Raman spectra of Inorganic and coordination compounds, Wiley Interscience, New York, 231 (1978).
18. R.S. Drago, Physical methods in inorganic chemistry, Affiliated East-West Press Pvt. Ltd., New Delhi, 162 (1968).
19. A.B.P. Lever, Inorganic Electronic Spectroscopy, 2<sup>nd</sup> ed. Elsevier, 507, 455 (1984).
20. Tanabe, Y. and Sugano, S., *J. Phys. Soc.*, **9**: 766 (1954).
21. Chandra, S. and Singh, R., *Indian J. Chem.*, **27A**: 417 (1988).
22. Kumar, B.K., Ravinder, V., Swamy, G.B. and Swamy, S.J. *Indian J. Chem.*, **33A**: 136 (1994).
23. A.B.P. Lever, *J. Chem. Edn.*, **45**, 711 (1966).
24. C.K. Jorgenson, *Proc. Inorg. Chem.*, **4**: 73 (1963).
25. Y. Tanabe and S. Sugano, *J. Phy. Soc.*, **9**: 766 (1954).
26. R.L. Dutta and A. Syamal, Elements of magnetochemistry, 2<sup>nd</sup> Ed., Affiliated East-West Press Pvt. Ltd., New Delhi, 232 (1993).
27. P.T. Manoharan, P.K. Mehrotra, M.M. Taquikhan and R.K. Andal, *Inorg. Chem.*, **12**: 2753 (1973).