

## Synthesis and characterization of the complexes of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) with 5-(2-hydroxybenzylidene)amino-benzopyrazole

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Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with 5-(2-hydroxybenzylidene)aminobenzopyrazole (HBAB) have been prepared and characterized. The IR spectral studies indicate that the ligand act as a bidentate donor and coordinates through the nitrogen of the azomethine group and deprotonated OH group. The complexes  $[M(HBAB)_3]$  ( $M = Cr, Fe$ ) and  $[M(HBAB)_2 \cdot 2H_2O]$  ( $M = Mn, Co, Ni$ ) have been assigned an octahedral geometry whereas  $Cu(HBAB)_2$  is proposed to be square-planar. The ligand field parameters,  $10Dq$  and  $B$  have also been calculated.

The chemistry of pyrazole and related ligand has been extensively investigated<sup>1-3</sup>. Benzopyrazole and its derivatives have been reported<sup>4,5</sup> to possess corrosion inhibition activities. Considerable interest has centred on the synthesis and structural studies on metal complexes of benzopyrazoles<sup>6</sup> and benzopyrazole-derived ligands in recent years<sup>7-9</sup>. Some antifungal transition metal chelates of analogous 2-(2'-hydroxybenzylidene)aminobenzimidazole ligand have recently been reported<sup>10</sup>. In this paper we describe the synthesis and characterization of a new ligand derived from 5-aminobenzopyrazole and salicylaldehyde and its complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II).

### Experimental

All the reagents were obtained commercially and used as such.

### Preparation of 5-(2-hydroxybenzylidene)amino-benzopyrazole and its complexes

The ligand was prepared from 5-aminobenzopyrazole (10g, 75.0 mmol) and salicylaldehyde (9.18g, 75.10 mmol) by usual condensation method. The complexes were prepared by mixing the aqueous solution of 2.10 mmol metal chlorides

and HBAB (4.21 mmol) in hot ethanol (50ml). The reaction mixture was magnetically stirred for 2-3 hr and concentrated gradually until the solid product appeared. In some cases, the solid appeared immediately after mixing. The complexes thus obtained were filtered, washed and dried *in vacuo*.

Analysis for metals was performed by standard methods<sup>11</sup>. Carbon, hydrogen and nitrogen were determined microanalytically. IR spectra ( $4000-200\text{ cm}^{-1}$ ) were recorded with a Perkin-Elmer spectrophotometer model 621. Magnetic moments were determined by a vibrating sample magnetometer model 155. Reflectance spectra were taken on a Carl-Zeiss VSU-2P spectrophotometer.

### Results and discussion

The analytical results and magnetic moments of the complexes are summarized in Table 1. The results of elemental analysis are in good agreement with the proposed formulae of the ligand and its complexes. The IR spectrum of the ligand shows a medium intensity band at  $3250-3200\text{ cm}^{-1}$  attributable to  $\nu N-H$  mode. A broad medium intensity band around  $3420\text{ cm}^{-1}$  is attributed to  $\nu OH$  (phenolic) mode. A strong band at  $1640\text{ cm}^{-1}$  is a characteristic of the azomethine ( $-HC=N-$ ) group. The present ligand has four potential coordinating positions; the unsaturated nitrogen atom of the heterocyclic ring, the nitrogen of the azomethine group and oxygen and nitrogen atoms of the OH and NH groups. A comparison of the IR spectra of complexes with the ligand shows a shift towards lower wavenumbers by  $20-40\text{ cm}^{-1}$  in  $\nu HC=N$  band which indicates coordination through the nitrogen lone pair<sup>12-14</sup>. The  $\nu C-O$  (phenolic) band in the ligand is observed at a relatively higher frequency at  $1500\text{ cm}^{-1}$  presumably due to the partial double bond character of the neighbouring benzene ring<sup>15</sup>. This band is shifted to  $1580-1575\text{ cm}^{-1}$  in its complexes indicating coordination through the oxygen atom of the hydroxyl group. Coordination through oxygen is further substantiated by the disappearance of the O-H deformation band of the ligand (at  $1400\text{ cm}^{-1}$ ) in these complexes. The C=N (heterocyclic ring) and N-H stretching frequencies appear at about the same positions. This rules out the possibility of coordination through

Table 1—Melting point, magnetic moment and analytical data of the complexes

Complex (% Yield)	M.P. (°C)	$\mu_{\text{eff.}}$ (B.M.)	Found (Calc.)(%)			
			C	H	N	M
$\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}$ (65)	218	—	70.6 (70.87)	4.9 4.67	17.6 17.7	— (—)
$\text{Cr}(\text{C}_{14}\text{H}_{10}\text{N}_3\text{O})_3$ (50)	275	3.68	66.7 (66.31)	4.1 3.97	16.8 16.5	6.9 6.83)
$\text{Mn}(\text{C}_{14}\text{H}_{10}\text{N}_3\text{O})_2\cdot 2\text{H}_2\text{O}$ (70)	230	5.94	59.8 (59.68)	3.7 3.57	14.8 14.91	9.9 9.75)
$\text{Fe}(\text{C}_{14}\text{H}_{10}\text{N}_3\text{O})_3$ (50)	250	5.83	65.8 (66.01)	3.8 3.95	16.7 16.49	7.4 7.25)
$\text{Co}(\text{C}_{14}\text{H}_{10}\text{N}_3\text{O})_2\cdot 2\text{H}_2\text{O}$ (50)	240	4.90	59.1 (59.26)	4.0 3.90	14.6 14.81	10.5 10.38)
$\text{Ni}(\text{C}_{14}\text{H}_{10}\text{N}_3\text{O})_2\cdot 2\text{H}_2\text{O}$ (55)	270	3.06	59.0 (59.29)	3.7 3.90	14.6 14.81	10.6 10.35)
$\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_3\text{O})_2$ (60)	260	1.89	62.5 (62.73)	3.9 3.76	15.3 15.67	11.5 11.85)

nitrogen atoms of these groups.

The non-ligand bands around 430-400 and 360-320  $\text{cm}^{-1}$  may be tentatively assigned to  $\nu_{\text{M-O}}$  and  $\nu_{\text{M-N}}$  modes, respectively. The bands at 900-800 and 650-610  $\text{cm}^{-1}$  in the Mn(II), Co(II) and Ni(II) complexes may be due to coordinated water.

In case of Cr(III) and Fe(III) complexes the observed magnetic moment values (3.68 and 5.83 BM) are quite close to the calculated value for an octahedral geometry. The reflectance spectrum of Cr(III) complex exhibits three bands at 36200, 24400 and 17300  $\text{cm}^{-1}$  assignable to  ${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$ ,  ${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$  and  ${}^4T_{2g}(F) \leftarrow {}^4A_{2g}$  transitions, respectively. For Fe(III) complex only two bands are observed at 23600 and 19100  $\text{cm}^{-1}$ . These bands may be assigned to  ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$  and  ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$  transitions, respectively in an octahedral field. Using a set of the assigned ligand field transitions on the appropriate Tanabe-Sugano diagram, we calculated  $10Dq$  and  $B$  values. The  $10Dq$  and  $B$  values for Cr(III) complex are 13010 and 520  $\text{cm}^{-1}$  respectively. Values of  $10Dq=10876$  and  $B=830 \text{ cm}^{-1}$  were obtained for Fe(III) complex.

The magnetic moment of the Mn(II) complex suggests that the compound has high-spin octahedral configuration. Three  $d-d$  transitions at 29000, 24200 and 20000  $\text{cm}^{-1}$  are assigned to  ${}^4A_{1g}(G) \leftarrow {}^6A_{1g}$ ,  ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$  and  ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}$ , respectively suggesting octahedral stereochemistry. The values of  $10Dq$  and  $B$  are found to be 10008 and 834  $\text{cm}^{-1}$ , respectively.

The magnetic moment for the Co(II) complex is 4.9BM, which cannot be used to distinguish be-

tween tetrahedral and octahedral configurations<sup>16</sup>. Its reflectance spectrum is typical of six-coordinated Co(II) and does not resemble tetrahedral Co(II) spectra which are reported<sup>17</sup> not to have ligand-field bands above 18000  $\text{cm}^{-1}$ . The lowest energy band at 9900  $\text{cm}^{-1}$  is assigned to  ${}^4T_{2g} \leftarrow {}^4T_{1g}$  transition ( $\nu_1$ ). The main band at 23200  $\text{cm}^{-1}$  may be assigned to  ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$  transition ( $\nu_3$ ). The position of the  $\nu_2$  band ( ${}^4A_{2g} \leftarrow {}^4T_{1g}$  transition) which is not observed in the spectrum has been calculated at 20718  $\text{cm}^{-1}$  by the relation  $\nu_2 = \nu_1 + 10Dq$ . The ligand-field parameters ( $10Dq=10818 \text{ cm}^{-1}$ ,  $B=950 \text{ cm}^{-1}$ ) calculated by reported method<sup>18</sup> and the  $\nu_2/\nu_1$  ratio (2.09) are consistent with the proposed octahedral structure. Using the relationship  $\lambda = -0.168B^2/Dq$ , we obtained  $|\lambda|$ -value of 140  $\text{cm}^{-1}$ . The lower value of  $|\lambda|$  compared to that of free ion ( $-170 \text{ cm}^{-1}$ ) suggests considerable orbital overlap. The value of the covalency parameters, ( $\gamma=80\%$ ) is close to the values reported for some N- and O-donor (84-86%) ligands<sup>19</sup>.

The electronic spectrum of the high-spin Ni(II) complex exhibits three ligand-field bands at 10270 ( $\nu_1=10Dq$ ), 17200 ( $\nu_2$ ) and 27000 ( $\nu_3$ )  $\text{cm}^{-1}$  assigned to the  ${}^3T_{2g} \leftarrow {}^3A_{2g}$ ,  ${}^3T_{1g} \leftarrow {}^3A_{2g}$  and  ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$  transitions, respectively suggesting octahedral field around Ni(II). The fact that  $\nu_2$  band is stronger than  $\nu_1$  agrees well with their assignment as octahedral structure. The  $\nu_2/\nu_1$  ratio is also well within the characteristic 1.5-1.7 range reported for octahedral Ni(II) complexes. The nephelauxetic parameter,  $B$  has been calculated to

be  $846\text{ cm}^{-1}$ . Compared to the free-ion value of  $-315\text{ cm}^{-1}$ , there is a reduction in the calculated<sup>20</sup>  $\lambda$ -value of  $-188\text{ cm}^{-1}$  for this complex which indicates significant orbital contribution and covalent character. The low  $\beta$  value of 0.80 signifies a fair amount of covalency in Ni-L bond.

Copper(II) complex has a magnetic moment value of 1.89BM frequently attributed to square-planar configuration. The solid reflectance spectrum of the Cu(II) complex displays two  $d-d$  transitions at  $15500$  and  $20300\text{ cm}^{-1}$  which may be assigned to the transitions.  ${}^2A_{1g} \leftarrow {}^2B_{1g}$  and  ${}^2E_g \leftarrow {}^2B_{1g}$  respectively assuming square-planar stereochemistry.

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