

## Synthesis and spectral studies of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II) complexes of 4-oxo-4H-1-benzopyran-3-carboxaldehyde hydrazone derivatives

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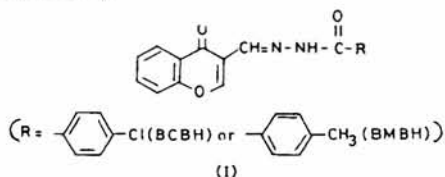
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A few complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with 4-oxo-4H-1-benzopyran-3-(carboxaldehyde-4-chlorobenzylhydrazone) (BCBH) and 4-oxo-4H-1-benzopyran-3-(carboxaldehyde-4-methylbenzylhydrazone) (BMBH) have been synthesised and characterized by elemental analysis, molar conductivities, magnetic measurements and IR and visible spectral studies. The IR spectra show that BCBH and BMBH behave as bidentate ligands either in the keto or enol form.

Hydrazides and hydrazones have been used widely as antituberculous compounds because of their ability to form metal chelates<sup>1,2</sup>. Metal chelates with hydrazone derivatives have been the subject of several investigations, the interest in such studies arising mainly from their structural aspects<sup>3</sup>. Also, there is some interest in the chemistry of 4-oxo-4H-1-benzopyran derivatives because of their ability to function as chelating agents, and thereby assist in the analytical determination of a large number of transition metal ions<sup>4</sup>.

The aim of this work is to study the role and activity of carbonyl group of both the benzopyran and hydrazone moieties towards complex formation (structure I).



### Materials and Methods

All the chemicals used were of BDH quality.

#### Preparation of ligands

The ligand 4-oxo-4H-1-benzopyran-3-carboxaldehyde was synthesised according to the literature method<sup>5,6</sup>. Its hydrazones, BCBH and BMBH, were prepared by refluxing an equimolar mixture of 4-oxo-4H-1-benzopyran-3-carboxaldehyde (8.71 g, 0.05 mol) and 4-chlorobenzoic acid hydrazide (8.5 g, 0.05 mol) or 4-methylbenzoic

acid hydrazide (7.5 g, 0.05 mol) in ethanol (50 ml) on a water bath for ~ 3h. The product was filtered off, washed with ethanol, recrystallized from absolute ethanol and finally dried in a vacuum desiccator over anhydrous calcium chloride. Yield: 11.3 g (69.2%), m.p. 202°C for BCBH and 11.8 g (77.05%), m.p. 189°C for BMBH.

#### Preparation of complexes

All the solid complexes were prepared by mixing the appropriate amounts of the ligands, BCBH and BMBH (1.0 mmol) in absolute ethanol (50 ml) to the solutions of 1.0 mmol of the hydrated metal(II) chloride, bromide or acetate, in absolute ethanol (50 ml). The mixtures were refluxed on a water bath for ~ 2-3 h when the solid complexes started precipitating. The yield increased as the reflux was continued. This method was applied for the preparation of all the complexes. To ensure the isolation of pure complexes, the reaction products were filtered immediately while the solution was still hot, washed with ethanol and diethyl ether and finally dried in a vacuum desiccator over anhydrous calcium chloride.

The analyses for metal and halides were carried out by standard methods<sup>7</sup>. Carbon, hydrogen and nitrogen analyses were performed by Microanalytical unit at University of Liverpool.

Magnetic moments were obtained at room temperature by the Gouy method using Hg[Co(SCN)<sub>4</sub>] as a calibrant. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer as nujol mulls between CsI plates.

Electronic spectra in DMSO were recorded using a Perkin-Elmer Lambda 38 spectrophotometer. Molar conductivities in DMSO ( $10^{-3}$  mol l $^{-1}$ ) at room temperature were measured using a YSI Model 32 conductivity bridge.  $^1\text{H}$  NMR spectra were recorded at ambient temperature on a Bruker WM250 multinuclear spectrometer (Uni-

versity of Liverpool). The water of hydration was determined by heating the hydrated complexes to 120°C.

### Results and Discussion

The analytical data of the metal complexes (Table 1) show that the complexes isolated were

Table 1—Analytical and physical data of the complexes derived from BCBH and BMBH

Compound Empirical Formula	Yield (%)	M.pt., (°C) Colour	Found (Calcd.), %					$\Lambda_m$ (ohm $^{-1}$ cm $^2$ mol $^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)
			C	H	N	M	X		
BCBH	69.2	202	62.35	3.18	8.47	—	—	—	5.23
C $_{17}$ H $_{11}$ N $_2$ O $_3$ Cl		white	(62.49)	(3.39)	(8.57)				
[Cu(BCBH)Cl(CH $_2$ O)]Cl	65.2	280	42.35	2.67	6.03	12.95	14.50	28.8	2.10
CuC $_{17}$ H $_{13}$ N $_2$ O $_4$ Cl $_3$		green	(42.61)	(2.73)	(5.84)	(13.26)	(14.80)		
[Cu(BCBH)Br(H $_2$ O)]Br	71.2	250	35.87	2.11	4.96	11.80	28.20	55.8	1.76
CuC $_{17}$ H $_{13}$ N $_2$ O $_4$ Br $_2$ Cl		green	(35.94)	(2.31)	(4.93)	(11.18)	(28.13)		
[Co(BCBH)Cl(H $_2$ O) $_3$ ]Cl	59.0	243	40.20	3.48	5.63	11.68	14.00	49.9	—
CoC $_{17}$ H $_{17}$ N $_2$ O $_6$ Cl $_3$		pink	(39.99)	(3.36)	(5.48)	(11.54)	(13.89)		
[Ni(BCBH)Cl(H $_2$ O)]Cl.H $_2$ O	68.2	> 300	41.30	3.05	5.53	11.60	14.67	60.5	3.58
NiC $_{17}$ H $_{13}$ N $_2$ O $_5$ Cl $_3$		green	(41.47)	(3.07)	(5.69)	(11.92)	(14.40)		
[Mn(BCBH)Cl(H $_2$ O)]Cl	76.6	> 300	43.20	2.60	6.25	11.40	15.24	44.7	6.49
MnC $_{17}$ H $_{13}$ N $_2$ O $_4$ Cl $_3$		yellow	(43.39)	(2.78)	(5.95)	(11.67)	(15.07)		
[Zn(BCBH)Cl $_2$ ].2H $_2$ O	57.0	268	40.59	3.04	5.63	13.46	14.80	4.5	—
ZnC $_{17}$ H $_{13}$ N $_2$ O $_5$ Cl $_3$		white	(40.91)	(3.03)	(5.61)	(13.10)	(14.21)		
[Cd(BCBH)Cl $_2$ ]	57.0	> 300	39.83	2.14	5.43	22.39	13.85	10.2	—
CdC $_{17}$ H $_{11}$ N $_2$ O $_3$ Cl $_3$		white	(40.03)	(2.17)	(5.49)	(22.04)	(13.90)		
[Hg(BCBH)Cl $_2$ ]	63.3	234	33.99	1.88	4.69	33.10	11.40	0.6	—
HgC $_{17}$ H $_{11}$ N $_2$ O $_3$ Cl $_3$		white	(34.13)	(1.85)	(4.68)	(33.53)	(11.85)		
[Co(BCBH - H) $_2$ ].2H $_2$ O	58.6	> 300	54.58	3.19	7.31	7.65	—	3.8	1.67
CoC $_{34}$ H $_{24}$ N $_4$ O $_8$ Cl $_2$		brown	(54.71)	(3.24)	(7.50)	(7.90)			
[Ni(BCBH - H) $_2$ (H $_2$ O) $_2$ ]	49.2	265	54.88	3.03	7.68	7.55	—	2.4	3.35
NiC $_{34}$ H $_{24}$ N $_4$ O $_8$ Cl $_2$		brown	(54.73)	(3.24)	(7.51)	(7.86)			
BMBH	77.05	189	70.39	4.52	9.05	—	—	—	—
C $_{18}$ H $_{14}$ N $_2$ O $_3$		yellow	(70.58)	(4.61)	(9.14)				
[Cu(BMBH)Cl(H $_2$ O)]Cl	65.5	244	47.29	3.17	6.32	13.52	15.00	35.1	2.13
CuC $_{18}$ H $_{16}$ N $_2$ O $_4$ Cl $_2$		green	(47.12)	(3.51)	(6.10)	(13.85)	(15.46)		
[Cu(BMBH)Br(H $_2$ O)]Br	67.7	266	40.01	2.70	5.10	11.40	29.20	52.5	1.69
			(39.48)	(2.94)	(5.11)	(11.60)	(29.18)		
[Mn(BMBH)Cl(H $_2$ O)]Cl	66.7	> 300	48.52	3.29	6.42	11.93	15.50	45.1	6.43
MnC $_{18}$ H $_{16}$ N $_2$ O $_4$ Cl $_2$		yellow	(48.03)	(3.58)	(6.22)	(12.20)	(15.75)		
[Zn(BMBH)Cl $_2$ ]	56.8	289	48.67	3.17	6.29	14.60	15.90	4.0	—
ZnC $_{18}$ H $_{14}$ N $_2$ O $_3$ Cl $_2$		white	(48.85)	(3.19)	(6.33)	(14.77)	(16.02)		
[Cd(BMBH)Cl $_2$ ]	63.3	> 300	44.43	2.72	5.53	23.03	14.60	9.8	—
CdC $_{18}$ H $_{14}$ N $_2$ O $_3$ Cl $_2$		white	(44.16)	(2.88)	(5.72)	(22.99)	(14.48)		
[Hg(BMBH)Cl $_2$ ]	50.8	239	37.37	2.40	4.86	34.55	12.20	0.6	—
HgC $_{18}$ H $_{14}$ N $_2$ O $_3$ Cl $_2$		white	(37.42)	(2.44)	(4.85)	(34.72)	(12.27)		
[Co(BMBH - H) $_2$ (H $_2$ O) $_2$ ]	64.9	> 300	61.09	4.27	8.17	8.34	—	6.8	4.46
CoC $_{36}$ H $_{30}$ N $_4$ O $_8$		brown	(61.28)	(4.29)	(7.94)	(8.35)			
[Ni(BMBH - H) $_2$ (H $_2$ O) $_2$ ]	58.8	255	61.05	4.70	7.73	7.90	—	3.2	2.70
NiC $_{36}$ H $_{30}$ N $_4$ O $_8$		brown	(61.30)	(4.29)	(7.94)	(8.32)			

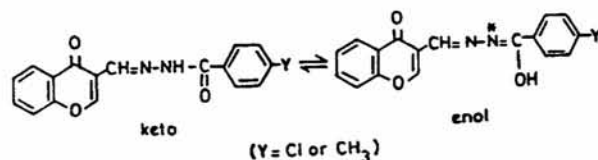
Table 2—Electronic bands and ligand field parameters of the complexes derived from BCBH and BMBH

Compound	Band Position (cm <sup>-1</sup> )	D <sub>q</sub>	B	β
[Co(BCBH)Cl(H <sub>2</sub> O) <sub>3</sub> ]Cl	16667, 20000	889.58	390.2	0.92
[Co(BCBH-H) <sub>2</sub> ].2H <sub>2</sub> O	12500, 21276	—	—	—
[Ni(BCBH)Cl(H <sub>2</sub> O)]Cl.H <sub>2</sub> O	14925, 22222	—	—	—
[Ni(BCBH-H) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	16667, 23529	1064.0	551.7	0.53
Mn(BCBH)Cl(H <sub>2</sub> O)]Cl	23809, 25000, 30769, 32154, 35714	—	—	—
[Cu(BCBH)Cl(H <sub>2</sub> O)]Cl	14225, 24510, 29199, 29499	—	—	—
[Cu(BCBH)Br(H <sub>2</sub> O)]Br	14205 (br), 24213, 29155	—	—	—
[Co(BMBH-H) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	14280, 19607 (sh), 22727	766.1	935.2	0.96
[Ni(BMBH-H) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	14286, 25000	863.86	891.4	0.86
[Mn(BMBH)Cl(H <sub>2</sub> O)]Cl	24390, 32051	—	—	—
[Cu(BMBH)Cl(H <sub>2</sub> O)]Cl	14085 (br), 23256, 24331, 33898	—	—	—
[Ni(BMBH)Br(H <sub>2</sub> O)]Br	13927, 31250, 33003	—	—	—

in keto and enol form and were of the types [Co(BCBH)Cl(H<sub>2</sub>O)<sub>3</sub>]Cl, [MLX(H<sub>2</sub>O)]X.nH<sub>2</sub>O (where M = Cu(II), Ni(II) or Mn(II), X = Cl or Br and n = 0 or 1), [MLCl<sub>2</sub>].nH<sub>2</sub>O (M = Zn(II), Cd(II) or Hg(II) and n = 0 or 2) and [M(L-H)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (M = Co(II) or Ni(II) and L = BCBH or BMBH).

All the metal complexes are stable in air and insoluble in common organic solvents, but easily soluble in DMF and DMSO. The molar conductivities in DMSO at 25°C (Table 1) indicate that complexes [Co(BCBH)Cl(H<sub>2</sub>O)<sub>3</sub>]Cl, [M(BCBH)X(H<sub>2</sub>O)]X [M = Cu(II); Ni(II) and Mn(II); X = Cl or Br] and [M(BMBH)X(H<sub>2</sub>O)]X [M = Cu(II) and Mn(II); X = Cl or Br] have high conductivity values which suggest that they are 1:1 electrolytes<sup>8</sup>. Also, the number of determined chloride ions<sup>7</sup> provides additional evidence for 1:1 electrolytes. The other complexes appeared to be non-electrolytic in nature.

BCBH and BMBH can be represented by two tautomeric forms, the keto and enol forms.

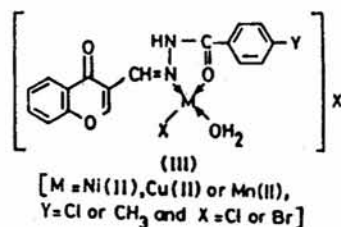
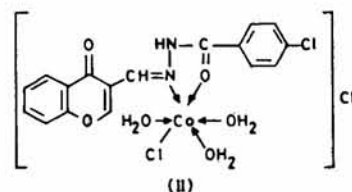


The <sup>1</sup>H NMR spectra of BCBH and BMBH show signals at δ13.66, 12.99 and 10.40, 10.32 ppm for the -NH- and -CH=N- protons, respectively<sup>9,10</sup>. The presence of -NH- signal in the spectra of BCBH and BMBH show the presence of the ligand in the keto form.

The infrared spectra also show that BCBH and BMBH exist mainly in keto forms. In the higher frequency region, a medium intensity band is ob-

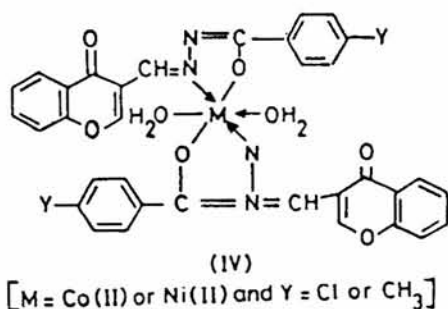
served at 3280 cm<sup>-1</sup> which may be due to νNH vibrations. Bands at 950 and 960 cm<sup>-1</sup> in BCBH and BMBH spectra respectively, are due to ν(N-N)<sup>12</sup> while the band at 1630 cm<sup>-1</sup> is attributed to ν(C=N)<sup>13,14</sup>. The spectra of two compounds show two bands each at 1645 and 1670 cm<sup>-1</sup> which are assignable to ν(C=O) of the benzopyran moiety<sup>15</sup> and ν(C=O) in the hydrazide residues, respectively. No bands exist above 3500 cm<sup>-1</sup>. All these observations are consistent with the keto form of the ligands.

A comparison of the IR spectra of BCBH and BMBH and their metal complexes shows that the two ligands form complexes in both keto and enol forms. In [Co(BCBH)Cl(H<sub>2</sub>O)<sub>3</sub>]Cl (structure II).



[M(BCBH)X(H<sub>2</sub>O)]X (M = Cu(II), Ni(II) or Mn(II) and X = Cl or Br) (structure III), [M(BCBH)Cl<sub>2</sub>].nH<sub>2</sub>O (n = 0 or 2) and [M(BMBH)Cl<sub>2</sub>] (M = Zn(II), Cd(II) and Hg(II)) complexes, the ligands react in the keto form. The ligands BCBH and BMBH be-

have as bidentate ligands, coordinating via the carbonyl oxygen (C=O) of the hydrazide moiety and the azomethine nitrogen (C=N) groups. This mode of chelation is supported by the following observation: (i) the shift of both  $\nu(\text{C}=\text{O})$  of the hydrazide moiety and  $\nu(\text{C}=\text{N})$  to lower wavenumbers and  $\nu(\text{N}-\text{N})$  shifts to higher wavenumber; (ii) the bands assignable to the  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{O})$  of the benzopyran moiety remain unchanged, indicating that these groups do not take part in coordination<sup>10,16</sup> and (iii) the appearance of new bands in the regions 535-550, 415-425 and 280-305  $\text{cm}^{-1}$  assigned to  $\nu(\text{M}-\text{O})$ <sup>17</sup>,  $\nu(\text{M}-\text{N})$ <sup>18</sup> and  $\nu(\text{M}-\text{X})$ <sup>19</sup>, respectively.



On the other hand, in  $[\text{M}(\text{BCBH}-\text{H})_2(\text{H}_2\text{O})_2]$  and  $[\text{M}(\text{BMBH}-\text{H})_2(\text{H}_2\text{O})_2]$  ( $\text{M} = \text{Co}(\text{II})$  or  $\text{Ni}(\text{II})$ ) complexes (structure IV) BCBH and BMBH react with metal acetates in the enol form. The ligands act as bidentate ligands coordinating via the azomethine nitrogen (C=N) and the enolic carbonyl oxygen ( $=\overset{\text{O}}{\text{C}}-\text{OH}$ ) with the displacement of hydrogen atom from the latter group. This mode of complexation is supported by the following evidence: (i) the disappearance of both  $(-\text{NH}-)$  and  $(\text{C}=\text{O})$  of the hydrazide moiety with the simultaneous appearance of new bands in the regions 1580-1585  $\text{cm}^{-1}$  and 1030-1055  $\text{cm}^{-1}$  assigned to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}-\text{O})$ <sup>18</sup>, respectively; (ii) the  $\nu(\text{C}=\overset{\text{O}}{\text{N}})$  shifts to lower wavenumber while  $\nu(\text{N}-\text{N})$  shifts to higher wavenumber; (iii) the appearance of new bands in the regions 550-555  $\text{cm}^{-1}$  and 415-425  $\text{cm}^{-1}$  assignable to  $\nu(\text{M}-\text{O})$ <sup>17</sup> and  $\nu(\text{M}-\text{N})$ <sup>18</sup>, respectively and (iv) the bands due to  $\nu(\text{C}=\text{O})$  of the benzopyran moiety remain unaltered, indicating that this group does not take part in coordination.

The spectra of all hydrated complexes, except  $[\text{Zn}(\text{BCBHCl}_2)_2 \cdot 2\text{H}_2\text{O}]$ , exhibit characteristic bands of coordinated water at *ca.* 3500, 1610, 890 and 770  $\text{cm}^{-1}$  assigned to  $\nu(\text{OH})$ ,  $\nu(\text{H}_2\text{O})$ ,  $\rho_r(\text{H}_2\text{O})$  and  $\rho_w(\text{H}_2\text{O})$  vibrations<sup>20</sup>, respectively.

The magnetic moments and electronic spectral data of the complexes are listed in Table 2.

The electronic spectra of the brown  $[\text{Co}(\text{BMBH}-\text{H})_2(\text{H}_2\text{O})_2]$  and pink  $[\text{Co}(\text{BCBHCl})_3(\text{H}_2\text{O})_3]\text{Cl}$  complexes show two bands at 14280, 16667 and 22727, 20000  $\text{cm}^{-1}$ , respectively, assigned to  ${}^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$  transitions, respectively, which are consistent with the octahedral geometry<sup>21</sup>. The magnetic moment values are near the spin only value for high-spin octahedral complexes. The value of magnetic moment (1.67 B.M.) of the  $[\text{Co}(\text{BCBH}-\text{H})_2] \cdot 2\text{H}_2\text{O}$  falls in the range reported for square-planar and/or low spin octahedral structures. The presence of characteristic band at 21276  $\text{cm}^{-1}$  supports the square-planar configuration<sup>21</sup>.

The electronic spectra of the brown  $[\text{Ni}(\text{BCBH}-\text{H})_2(\text{H}_2\text{O})_2]$  and  $[\text{Ni}(\text{BMBH}-\text{H})_2(\text{H}_2\text{O})_2]$  complexes are consistent with octahedral geometry showing two bands at 16667, 16225 and 23529, 25000  $\text{cm}^{-1}$ , assignable to the transition  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$  respectively.

The calculated values of  $D_q$ ,  $B$ ,  $\beta$  and  $\nu_2/\nu_1$  lie in the same range as reported for octahedral coordinated Ni(II) ion<sup>22</sup>. The  $\beta$  values show a trend to covalent bonding. Also, the magnetic moment values (3.35-2.7 B.M.) are additional evidence for an octahedral structure for the two complexes. The electronic spectrum of  $[\text{Ni}(\text{BCBHCl})(\text{H}_2\text{O})]\text{Cl}$  is consistent with tetrahedral geometry showing one band at 14925  $\text{cm}^{-1}$  assignable to  ${}^3T_1(F) \rightarrow {}^3A_2(F)$  and a band at 22222  $\text{cm}^{-1}$  corresponding to an excited state derived from the  ${}^1G$  term<sup>23</sup>. The lowering in  $\mu_{\text{eff}}$  (3.5 B.M.) than the expected value (4.1 B.M.) may be due to the effect of covalency and/or distortion.

The copper (II) complexes have magnetic moment values indicating the presence of Cu(II) ion. The higher values of the magnetic moments may be attributed to the ionic nature of the complexes. The electronic spectra of these complexes show a broad band at 13927-14224  $\text{cm}^{-1}$ . The position of the bands indicate that these complexes have a square planar stereochemistry<sup>21</sup> and can be assigned to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions in the increasing order of energy. The high energy bands in the region 24000-31000  $\text{cm}^{-1}$  may be assigned to ligand-metal charge transfer transition.

The  $\mu_{\text{eff}}$  values for the  $[\text{Mn}(\text{BCBHCl})(\text{H}_2\text{O})]\text{Cl}$  and  $[\text{Mn}(\text{BMBHCl})(\text{H}_2\text{O})]\text{Cl}$  complexes are as expected for high spin  $d^5$  system. The electronic spectra of the two complexes show mainly two bands at 23809, 24390 and 30769, 32051  $\text{cm}^{-1}$ , respectively. The two clearly observed bands indicate tetrahedrally coordinated Mn(II) (ref. 24).

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