

## Synthesis and characterization of metal complexes with a schiff base formed by condensation of S-benzyl dithiocarbazate with isatin ( $H_2IBD$ )

G M Abu El-Reash\*, Fim Taha, A M Shallaby & O A El-Gamal  
Chemistry Department, Faculty of Science,  
Mansoura University, Mansoura, Egypt

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Synthesis and characterization of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Hg(II) and  $UO_2^{2+}$  complexes of isatin-hydrazone-S-benzylthiocarbazate ( $H_2IBD$ ) are reported. Elemental analysis, molar conductance, magnetic moment and spectral (IR, visible, NMR) data have been used to characterize the complexes. IR spectral data show that the ligand behaves in a bidentate, tridentate or tetradentate manner in different complexes. An octahedral structure is proposed for the Mn(II), Co(II) and Ni(II) complexes while a square-planar structure is proposed for Cu(II) complexes on the basis of magnetic and spectral measurements.

Studies on metal complexes of thio-schiff bases containing S-benzylthiocarbazate have been reported<sup>1-7</sup>. These ligands as well as their metal complexes are frequently used as anticancer<sup>8</sup>, antibacterial<sup>9</sup> and antifungal<sup>10</sup> agents. In continuation of our interest in the ligational behaviour of nitrogen, oxygen and sulphur donor schiff bases, we describe here new metal complexes of isatin hydrazone-S-benzylthiocarbazate. The existing literature on the coordination chemistry of this ligand is obscure.

All the chemicals used were of AR grade. The hydrazone-S-benzylthiocarbazate was synthesized according to the general literature method<sup>11</sup>. The schiff base was prepared by heating equimolar amounts of the isatin (14.7 g, 0.1 mol) and the S-benzylthiocarbazate (20 g, 0.1 mol) in 100 ml ethanol under reflux for 1 hr. The yellow crystals which separated were recrystallized from benzene; m.p. 231°C; yield 28.6 g, 82% [Found; C, 58.5; H, 3.8. Req'd. for  $H_2IBD$ : C, 58.7; H, 4.0%].

### Preparation of the complexes

The complexes were prepared by refluxing equimolar amounts of  $H_2IBD$  (3.27 g, 0.01 mol) in 50 ml absolute ethanol and hydrated metal chloride or uranyl acetate (0.01 mol) in 20 ml absolute ethanol, but the other acetate salts of Cu(II), Zn(II) and

Cd(II) (0.01 mol) were dissolved in 30 ml doubly distilled water for 1-2 hr. The product was filtered off, washed with hot ethanol, then with diethyl ether and dried *in vacuo*. The solid complexes were heated in an electric oven for 3 hr at 120°C.

All the measurements were carried out as reported earlier<sup>12</sup>.

### Results and discussion

The analytical and physical data for the metal complexes are listed in Table 1. The complexes are quite stable in air and insoluble in common organic solvents but soluble in DMF and DMSO. The molar conductivities in DMF solution (6-30  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ) indicate a nonelectrolytic nature for all of the complexes<sup>13</sup>.

The IR spectrum of  $H_2IBD$  in KBr shows two bands at 1700 and 1580  $\text{cm}^{-1}$  which can be assigned to  $\nu(\text{CO})$  and  $\nu(\text{C}=\text{N})$ , respectively. The bands at 1480, 1255, 1020 and 680  $\text{cm}^{-1}$  are due to thioamide-I, -II, -III and -IV bands<sup>14</sup>, respectively. The bands assigned to thioamide vibrations are not pure and have substantial contributions from  $\nu(\text{C}-\text{N})$ ,  $\delta(\text{C}-\text{H})$ ,  $\delta(\text{N}-\text{H})$  and  $\nu(\text{C}-\text{S})$  vibrations<sup>15</sup>. The doublets at 2900 and 2960  $\text{cm}^{-1}$  are attributed to the symmetric and asymmetric stretching vibrations of the  $-\text{S}-\text{CH}_2-\text{Ph}$  grouping, which are reduced to a weak doublet in the IR spectra of the complexes. In addition, two bands at 3180 and 3140  $\text{cm}^{-1}$  are assigned to the  $\nu(\text{NH})$  of isatin and S-benzyl moiety, respectively. The broad but weak bands in the regions 1960-1900 and 2360-2280  $\text{cm}^{-1}$ , mainly due to  $\text{O}\cdots\text{H}-\text{N}$  stretching vibrations<sup>16,17</sup>, indicate intramolecular hydrogen bonding between oxygen of isatin moiety and the NH group as shown in structure (I). No bands due to SH and OH stretching modes are observed near 2570 and 3400, respectively. The absence of these bands indicates the presence of  $H_2IBD$  in the thione and keto form.

The NMR spectrum of  $H_2IBD$  in  $\text{DMSO}-d_6$  shows four signals at  $\delta = 4.6, 6.9-7.14, 7.3-7.6$  and 11.4 ppm relative to TMS which may be assigned to the methylene protons of the S-benzyl moiety

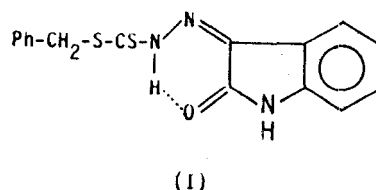


Table 1—Analytical and physical data of H<sub>2</sub>IBD and its metal complexes

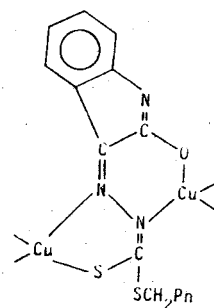
Compound (Yield, %)	Colour, (mp., °C)	Found (Calc.), %				$\mu_{\text{eff}}$ (BM)
		C	H	M	Cl	
[Mn(HIBD)Cl(H <sub>2</sub> O) <sub>3</sub> ] (56)	Deep violet (> 300)	41.2 (40.8)	3.34 (3.85)	10.8 (11.7)	7.6 (7.5)	5.76
[Co(HIBD) <sub>2</sub> ] (64)	Brown (200d)	54.2 (54.0)	3.8 (3.4)	8.0 (8.3)	—	4.73
[Ni(HIBD) <sub>2</sub> ] (82)	Brown (198d)	53.7 (54.0)	3.6 (3.4)	8.1 (8.3)	—	3.20
[Cu(HIBD)Cl] (78)	Brown (> 300)	44.9 (45.2)	3.1 (2.8)	14.3 (14.9)	8.8 (8.3)	1.85
[Cu(IBD)] (86)	Brown (215d)	50.6 (49.4)	3.1 (2.9)	15.8 (16.3)	—	1.50
[Cd(HIBD) <sub>2</sub> ] (60)	Orange (> 300)	50.4 (50.2)	3.6 (3.2)	13.9 (14.6)	—	—
[Cd(HIBD)Ac] (68)	Orange	43.1 (43.4)	3.6 (3.0)	22.4 (21.6)	—	—
[Zn(HIBD) <sub>2</sub> ] (48)	Orange (234)	53.7 (53.5)	2.3 (1.96)	8.8 (9.1)	—	—
[Zn(HIBD)Ac] (66)	Orange (> 300)	48.2 (48.0)	3.7 (3.4)	14.8 (14.5)	—	—
[Hg(HIBD) <sub>2</sub> ] (54)	Reddish-orange (289)	— (45.0)	— (2.8)	24.3 (23.5)	—	—
[UO <sub>2</sub> (H <sub>2</sub> IBD)Ac <sub>2</sub> ] (73)	Red (> 300)	33.9 (33.6)	3.1 (2.7)	36.9 (37.8)	—	—

(-S-CH<sub>2</sub>-Ph), the aromatic protons of both isatin and phenyl rings overlapped with the imino proton (-NH-C-) and the NH proton of isatin resi-



due, respectively.

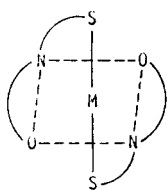
The IR spectrum of Cu(IBD) complex, which was prepared from the acetate salt, shows that H<sub>2</sub>IBD behaves as binegative tetradentate ligand, coordinating through the enolic oxygen and the nitrogen of the NH group from one end, and the thiol sulphur atom and the nitrogen atom of the C=N group on the other, with loss of two protons. Steric factors prevent the coordination of all the donors in a ligand molecule to a single metal ion; therefore, the ligand must act as a bridging unit between two metal centres, giving a polymeric structure as shown in structure (II). This mode of complexation is confirmed by the following evidences: (i) the disappearance of the  $\nu(\text{C}=\text{O})$ , the  $\nu(\text{NH})$  and the clear change in thioamide bands; and (ii) the appearance of new bands at 1625, 1590, 1320 and 655 cm<sup>-1</sup> due to  $\nu(\text{S}-\text{C}=\text{N})$ ,  $\nu(\text{O}-\text{C}=\text{N})$  cyclic,  $\nu(\text{C}-\text{O})$  and  $\nu(\text{C}-\text{S})$  modes.



(11)

In the [Cu(HIBD)Cl], [Ni(HIBD)<sub>2</sub>] and Co(HIBD)<sub>2</sub> complexes, the ligand (H<sub>2</sub>IBD) behaves as a mononegative tridentate ligand coordinating via the CO, the C=N and the CS in the thiol form after its deprotonation as shown in structure (III). This mode of complexation is suggested by the shift of both  $\nu(\text{CO})$  and  $\nu(\text{C}=\text{N})$  to lower wavenumbers ( $\sim 20$  cm<sup>-1</sup>), the disappearance of  $\nu(\text{CS})$  and the appearance of new bands at 1620 and 660 cm<sup>-1</sup> due to  $\nu(\text{S}-\text{C}=\text{N})$  and  $\nu(\text{C}-\text{S})$ .

In addition, H<sub>2</sub>IBD behaves as a mononegative bidentate ligand coordinating via the C=N and the



M = Ni(II) and Co(II)

(111)

CS in the thiol form. This behaviour, which is found in the  $[\text{Mn}(\text{HIBD})\text{Cl}(\text{H}_2\text{O})_3]$ ,  $[\text{Zn}(\text{HIBD})_2]$ ,  $[\text{Zn}(\text{HIBD})\text{Ac}]$ ,  $[\text{Cd}(\text{HIBD})_2]$  and  $[\text{Hg}(\text{HIBD})_2]$  complexes, is revealed by (i) the disappearance of  $\nu(\text{CS})$  and appearance of new bands at 1620 and 665  $\text{cm}^{-1}$  due to  $\nu(\text{S}-\text{C}=\text{N})$  and  $\nu(\text{C}-\text{S})$ , and (ii) the shift of  $\nu(\text{CN})$  to lower wavenumber (10  $\text{cm}^{-1}$ ); the shift of  $\nu(\text{CO})$  to higher wavenumber shows that CO group does not participate in the complexation. The bands observed at 3440, 1610, 890 and 770  $\text{cm}^{-1}$  in the IR spectrum of the complex  $[\text{Mn}(\text{HIBD})\text{Cl}(\text{H}_2\text{O})_3]$  complex are 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>18</sup> respectively of the coordinated water molecules. On drying this complex by heating in an oven up to 120°C no water molecule is removed which indicates the presence of water molecules in the coordination sphere.

In the  $\text{UO}_2(\text{H}_2\text{IBD})\text{Ac}_2$  complex,  $\text{H}_2\text{IBD}$  behaves as a neutral bidentate ligand coordinating via the CO and CN groups since both  $\nu\text{CO}$  and  $\nu\text{CN}$  modes shift to lower wavenumbers. The NMR spectrum shows new signals at 2.3-2.7 ppm due to  $\text{CH}_3$ -protons of the acetate group and the signal due to NH proton of isatin residue is shifted to 10.4 ppm as a result of the participation of CO in coordination. The uranyl complex exhibits three bands at 930, 840 and 265  $\text{cm}^{-1}$  assigned to  $\nu_3$ ,  $\nu_1$  and  $\nu_4$  modes, respectively, of the dioxouranium ion<sup>19</sup>. The force constant ( $F$ ) for bonding sites of the  $\text{U}=\text{O}$  vibration was calculated by the method of McGlynn *et al.*<sup>20</sup>, as 7.14  $\text{mdynes } \text{Å}^{-1}$ .

New bands observed in the complexes at 580-520, 485-450, 315-310 and 310-270  $\text{cm}^{-1}$  are tentatively assigned to the  $\nu(\text{M}-\text{O})$ <sup>21</sup>,  $\nu(\text{M}-\text{N})$ <sup>22</sup>,  $\nu(\text{M}-\text{S})$ <sup>21</sup> and  $\nu(\text{M}-\text{Cl})$ <sup>23</sup> modes.

The magnetic moments of the complexes are listed in Table 1. The electronic spectrum (DMF) of  $[\text{Mn}(\text{HIBD})\text{Cl}(\text{H}_2\text{O})_3]$  complex, shows two bands at 22220 and 27780  $\text{cm}^{-1}$  assignable to  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$  transitions<sup>24</sup>, respectively. The  $Dq$ ,  $B$  and  $\beta$  values are 1018.4, 925.8 and 0.96  $\text{cm}^{-1}$ , respectively suggesting the octahedral geometry<sup>25,26</sup>. In addition the magnetic mo-

ment (5.76 BM) can be taken as additional evidence for the octahedral structure. On increasing delocalization,  $\beta$  decreases and becomes less than unity in the complex.

The magnetic moment value (4.73 BM) for the  $[\text{Co}(\text{HIBD})_2]$  complex is near the value expected for high spin octahedral Co(II) complexes. The electronic spectrum (DMF) shows strong band at 22220  $\text{cm}^{-1}$  ( $\epsilon = 30.9$ ) and shoulder around 20000  $\text{cm}^{-1}$  assigned to the  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  ( $\nu_3$ ) transition<sup>27</sup>. The lowest bands  $\nu_2$  and  $\nu_1$  could not be observed in our instrument and thereby the ligand field parameters could not be calculated. The broad band at 26315  $\text{cm}^{-1}$  ( $\epsilon = 101$ ) is assigned to charge-transfer probably of the type  $\text{H}_2\text{IBD} \rightarrow \text{Co}$ .

The electronic spectrum (DMF) of  $[\text{Ni}(\text{HIBD})_2]$  shows a broad band centered at 19880  $\text{cm}^{-1}$  due to the  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) ( $\epsilon = 17$ ) transition. Also, a broad band at 26315  $\text{cm}^{-1}$  is observed which may be due to  $\nu_3$  transition [ ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ ] ( $\epsilon = 850$ ) or a charge transfer transition<sup>28</sup>. The value of its magnetic moment (3.2 BM) is an evidence for an octahedral structure.

The magnetic moments of  $[\text{Cu}(\text{HIBD})\text{Cl}]$  and  $[\text{Cu}(\text{IBD})]$  are 1.85 and 1.5 BM respectively at room temperature. The value observed for  $[\text{Cu}(\text{HIBD})\text{Cl}]$  is in the range for high spin Cu(II) complexes having monomeric structures<sup>29</sup>. The lowering of  $\mu_{\text{eff}}$  value in the case of  $[\text{Cu}(\text{IBD})]$  may be attributed to the polymeric structure. The electronic spectra of these complexes show bands at 14490, 23260 and 27027  $\text{cm}^{-1}$  for the former and at 15150, 16666, 17450, 22730 and 25970  $\text{cm}^{-1}$  for the latter. The positions of the bands indicate that these complexes have a square-planar stereochemistry<sup>28</sup>. The appearance of a high energy band at 22000-27000  $\text{cm}^{-1}$  may be due to polymeric structure or charge transfer phenomenon.

Finally, the U.V.- spectrum of the  $\text{UO}_2(\text{H}_2\text{IBD})\text{Ac}_2$  shows a band at 21270, 22222  $\text{cm}^{-1}$  assigned to  ${}^1E_g^+ \rightarrow \pi_u^3$ . This band is similar to the OOU symmetric stretching frequency for the first excited state<sup>30</sup>.

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## NOTES

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