

# Monomeric Nickel(II) Complexes with Tetradentate Bis(benzimidazole) Ligands; Synthesis, Spectral and $^1\text{H}$ and $^{13}\text{C}$ NMR Studies

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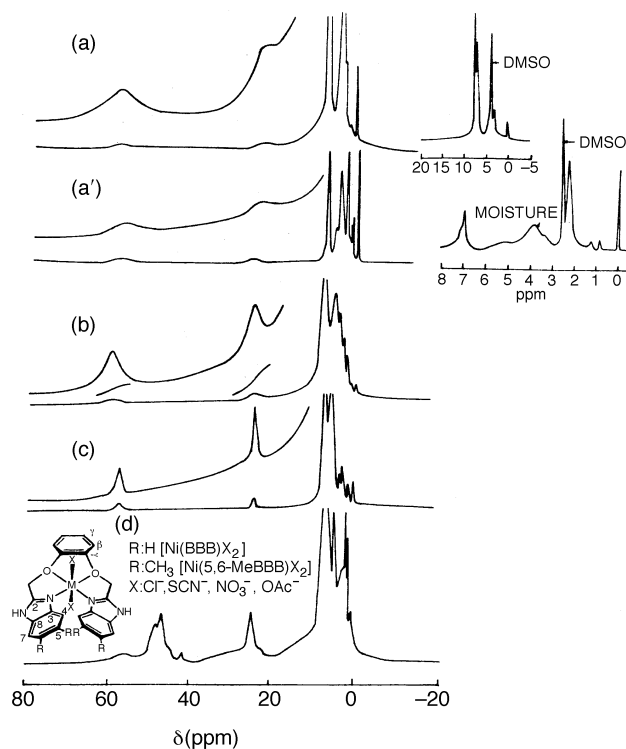
The tetradentate ligand 1,2-bis(2-benzimidazolylloxamethyl)benzene (BBB) is used to synthesize complexes of stoichiometry  $[\text{Ni}(\text{BBB})\text{X}_2]$  where  $\text{X} = \text{Cl}, \text{NCS}, \text{NO}_3$  or  $\text{OAc}$ ;  $^1\text{H}$  and  $^{13}\text{C}$  NMR has been used to assign the aliphatic and ring protons/carbons.

A variety of nickel(II)-containing proteins have the nickel(II) ion in a distorted octahedral environment with the imidazole nitrogen of the histidine amino acids as one of the coordinating atoms.<sup>9–11</sup> Keeping this in mind we were prompted to synthesize the present series of nickel(II) complexes with the 1,2-bis(2-benzimidazolylloxamethyl)benzene (BBB) ligand which provides an  $\text{N}_2\text{O}_2$  donor environment around the nickel(II) ion. The complexes isolated in the present study were  $[\text{Ni}(\text{BBB})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ni}(5,6\text{-MeBBB})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ni}(\text{BBB})(\text{NCS})_2]$ ,  $[\text{Ni}(\text{BBB})(\text{NO}_3)_2]$  and  $[\text{Ni}(\text{BBB})(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$ : these are respectively, orange, bluish, greenish blue, light-greenish blue and light bluish in colour. The complexes are air stable and decompose above  $300^\circ\text{C}$ .

Fig. 1(a)–(d) shows the  $^1\text{H}$  NMR spectra of the nickel(II) complexes, for which a tentative structure is shown in the inset; the chemical shifts for the complexes are shown in Table 2, along with proposed assignments. Table 3 gives the  $^{13}\text{C}$  chemical shift values for ligand and nickel(II) complexes (see full text).

The  $^1\text{H}$  NMR spectra of the present series of nickel(II) complexes reveal isotropically shifted signals between 0.0 and  $+59.0$  ppm at  $25^\circ\text{C}$  in  $[\text{D}_6]^{13}\text{C}$  DMSO solution. All the nickel(II) complexes show a resonance peak in the range of  $+56.0$  to  $+59.0$  ppm downfield with respect to TMS which shows a loss in intensity upon the addition of a drop of  $\text{D}_2\text{O}$  to the solution of complexes in  $[\text{D}_6]^{13}\text{C}$  DMSO, suggesting that the proton representing this peak could be easily exchanged. Such a proton in our ligating system is the N–H proton of the imidazole ring. Two such protons are present in the nickel(II) complexes; earlier studies have also identified this proton in the same chemical shift region.<sup>14</sup>

The next isotropically shifted resonance is found in the range of  $+23.0$  to  $+28.0$  ppm downfield with respect to TMS. It is interesting to compare the integrated intensity of this resonance with that identified for the two N–H protons, which is found to be in 3:1 ratio in all the com-



**Fig. 1**  $^1\text{H}$  NMR spectra of (a)  $[\text{Ni}(\text{BBB})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ; (a')  $[\text{Ni}(5,6\text{-MeBBB})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ , (b)  $[\text{Ni}(\text{BBB})(\text{NCS})_2]$ ; (c)  $[\text{Ni}(\text{BBB})(\text{NO}_3)_2]$ , (d)  $[\text{Ni}(\text{BBB})(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$

plexes; it may be concluded that the resonance at *ca* 24.0 ppm is indicative of six protons. The line widths of these two signals are comparable in most cases and thus it is reasonable to utilise relative integrated intensities in the present case as a measure of proton ratio.<sup>15</sup> It is estimated that those protons which are in close proximity to the nickel(II) centre would contribute to the resonance at *ca* 24 ppm; four

**Table 2** Proton contact shifts for ligand and nickel(II) complexes in  $[\text{D}_6]^{13}\text{C}$  DMSO solution at  $25^\circ\text{C}$

| Assignment (free ligand)                   | 5,6-MeBBB · H <sub>2</sub> O | BBB · H <sub>2</sub> O | Tentative assignment (complex)             | $[\text{Ni}(\text{BBB})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ | $[\text{Ni}(5,6\text{-MeBBB})\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ | $[\text{Ni}(\text{BBB})(\text{NCS})_2]$ | $[\text{Ni}(\text{BBB})(\text{NO}_3)_2]$ | $[\text{Ni}(\text{BBB})(\text{OAc})_2] \cdot 2\text{H}_2\text{O}$ |
|--|------------------------------|------------------------|--|--|--|---|--|---|
| NH   | —                            | 12.6 (2 H)             | NH   | 57.2 (2 H)   | 57.6 (2 H)   | 58.8 (2 H)                              | 57.6 (2 H)                               | 58.4 (2 H)  |
| OCH <sub>2</sub> (aliphatic)               | 5.3 (s, 4 H)                 | 5.3 (s, 4 H)           | OCH <sub>2</sub> C4(H)                     | 23.6 (6 H)   | 24.0 (6 H)   | 24.3 (6 H)                              | 24.0 (2 H)                               | 24.8 (6 H)  |
| C4(H), C7(H)                               | 7.3 (s, 4 H)                 | 7.6 (4 H)              | —  | —  | —  | —                                       | —  | —   |
| C5(H), C6(H)                               | —                            | 7.2 (4 H) <sup>a</sup> | C5(H), C6(H)                               | 7.2  | —  | 7.2                                     | 7.2                                      | 7.2   |
| C5(CH <sub>3</sub> ), C6(CH <sub>3</sub> ) | 2.3 (s, 12 H)                | —                      | C5(CH <sub>3</sub> ), C6(CH <sub>3</sub> ) | —  | 2.3 (s, 12 H)  | —                                       | —  | —   |
| Benzene β(H), γ(H)                         | 7.1 (m, 2 H)                 | 7.2 (2 H) <sup>a</sup> | Benzene β(H), γ(H)                         | 7.0  | 7.0  | 6.9                                     | 7.1                                      | 6.9   |
|  | 6.9 (m, 2 H)                 | 7.0 (2 H)              |  |  |  |   |  |   |

<sup>a</sup>δ 7.2 (s, 6 H).

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of the methylene protons of the aliphatic chain together with two protons from the C4(H) benzimidazole ring are likely candidates to contribute to this signal. This would also match the ratio of integrated intensities. Similar assignments have previously been made for related iron(III) and nickel(II) benzimidazole complexes.<sup>16–18</sup>

To assign the C5(H) and C6(H) protons in the benzimidazole ring we prepared 5,6-MeBBB. The NMR spectra shows a peak missing at +7.2 ppm and in its place a new peak, integrated to twelve protons, arises at +2.3 ppm; this resonance is therefore assigned to the protons of the methyl groups at positions 5 and 6 of the benzimidazole ring.

The NMR spectra of the nickel(II) complexes with this 5,6-dimethylsubstituted ligand [Fig. 1(a')] show that there is no change in the position and intensity of the signal at *ca* +57.0 ppm and *ca* +24.0 ppm, further substantiating that the above signals do not have any contribution from the C5(H) and C6(H) protons. Moreover the NMR spectrum shows the presence of a new peak at +2.3 ppm identical to that observed for the free ligand. This substitution experiment clearly indicates that the resonance arising at +7.2 ppm in the nickel(II) complexes with unsubstituted ligand (BBB) can be assigned to the C5(H) and C6(H) protons which do not undergo any contact shift in contrast to that observed for the C4(H) proton. The above observation indicates that a competing mechanism, having a sign opposite to that of a  $\sigma$  delocalisation pathway, is also operative in the present series of nickel(II) complexes leading to a near zero contact shift for the C5(H) and C6(H) protons.

In the case of [Ni(BBB)(OAc)<sub>2</sub>] [Fig. 1(d)] a new peak is observed between 46.0 to 48.0 ppm downfield with respect to TMS. This peak integrates to six protons and is assigned to the protons of two acetate groups bound to the nickel(II) centre. The splitting of this peak indicates that the protons of the two bound acetates are in a slightly differing chemical environment [Fig. 1(d) inset]. The above integrated ratio of protons confirms that, if water molecules are present they are unable to replace the bound anionic ligand, a fact which is corroborated by the molar conductance value of the above complex, which is  $0.0041 \Omega^{-1} \text{m}^2 \text{mol}^{-1}$ , implying a non-ionic complex in solution. Furthermore no IR band has been observed for bound hydroxy groups and TGA experiments show mass losses commensurate with only water of crystallization.

No doubling of peaks are observed in the NMR spectra, which indicates that the benzimidazole rings experience an equivalent ligand field environment in the present series of nickel(II) complexes. Such a pattern has been observed for complexes which have a mirror plane symmetry.<sup>19</sup>

In the <sup>13</sup>C NMR spectra of the nickel(II) complexes the peak observed at 140–145 ppm is therefore tentatively assigned to the C(2) of imidazole followed by the C(8) and C(9) carbons of the fused benzimidazole ring. The remaining relatively sharp peaks at 110 to 122 ppm and 105 to 112 ppm are assigned to the C(5) and C(6) and C(4) and C(7) carbons, respectively. The broad peak at 70 to 100 ppm is proposed to be due to the (CH<sub>2</sub>) methyl carbon of the aliphatic chain. This carbon not being the part of benzimidazole ring system is shifted *ca* +20 to +30 ppm downfield with respect to the free ligand and TMS. It has been shown earlier that if the spin polarization effect in the  $\pi$  framework of a ligand is the important mechanism in controlling the shifts then the contact shifts experienced by the ring carbons is of the opposite sign to the contact shifts experienced by the ring protons.<sup>21</sup>

The solution spectrum of the above complex shows d–d bands in the visible part of the spectrum in the 410–420 nm, 690 and in the 750–790 nm region. The splitting of a single band into two bands in the 690–790 nm region is indicative of a lowered site symmetry and could be attributed to steric interaction caused by the benzimidazole rings.

Infrared spectra of the complexes show that the band at *ca.* 1460 cm<sup>-1</sup> assigned to  $\nu(\text{C}=\text{N}-\text{C}=\text{C})$  in the free ligand, shifts by *ca.* 20 cm<sup>-1</sup> in the metal complexes, indicating direct coordination of the imine nitrogen atom to Ni<sup>II</sup>, as found for other metal complexes with benzimidazoles.<sup>27</sup> The thiocyanato complex shows a band at *ca.* 2100 cm<sup>-1</sup> characteristic of a coordinated NCS ligand. For the nitrate complex, three bands are observed at *ca.* 1300, 1010 and 990 cm<sup>-1</sup> characteristic of monodentate nitrate bound to nickel,<sup>28</sup> whereas in the acetato complex two strong bands appear at *ca.* 1540 and 1320 cm<sup>-1</sup> and are assigned to the unidentate binding of the acetate group.<sup>29</sup>

Techniques used: <sup>1</sup>H and <sup>13</sup>C NMR, IR, UV–VIS

Refs: 29

Figs: 3

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