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Characterisation of a mixed N-heterocycle, 2-(N-methylimidazole-2'-yl-thiomethyl)benzimidazole, and its complexes with nickel(II) and copper(II)

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2-(N-methylimidazole-2′-yl-thiomethyl)benzimidazole (L) has been synthesised and the complexes $[ML_2(ClO_4)_2]\cdot 2H_2O$ (M = Ni or Cu) and $[MLX_2]nH_2O$ (M = Cu, X = Cl or Br, n = 0; M = Ni, X = Cl, n = 3; M = Ni, X = Br, n = 0) prepared and characterised. Proposed geometries for the complexes are: octahedral geometry for perchlorate complexes; tetrahedral geometry for chloro-and bromo-complexes; dimeric square pyramidal for the chloro-complex of copper(II).

Keywords: methyl imidazole, benzimidazole, nickel, copper, perchlorate.

The chemistry of imidazole/benzimidazole and their derivatives is important in view of the presence of these moieties in biological systems.[1] The coordination of the metal to imidazole nitrogen and thioether sulfur in these systems has prompted the synthesis of imidazole/benzimidazole- and sulfur-containing ligands and their complexes. Such compounds may prove useful as structural and functional models in the study of active centres in biological systems. We report here studies on the synthesis and characterisation of complexes of one such sulfur-containing mixed N-heterocycle, 2-(N-methylimidazole-2'-yl-thiomethyl) (L) (Fig. 1) with salts of Ni(II) and Cu(II).

Experimental

All the chemicals were AR grade. Solvents were purified by the usual methods before use. The metal perchlorates were prepared by dissolving the corresponding metal carbonates in 1:1 perchloric acid and evaporating the resulting solution carefully to near dryness under reduced pressure. The precursor, 2-(chloromethyl)benzimidazole was prepared according to the reported procedure and 2-mercapto-N-methylimidazole was procured from Aldrich, USA.

Synthesis of 2-(N-methyl imidazole-2'-yl-thiomethyl) benzimidazole (L)

A mixture of 2-mercapto-N-methylimidazole (0.114 g, 1 mmol) and sodium hydroxide (0.004 g, 1 mmol) in ethanol (10 cm^3) was stirred under dinitrogen for 30 min. An ethanol solution (10 cm^3) of 2-(chloromethyl)benzimidazole (0.166 g, 1 mmol) was added slowly with stirring and the mixture was refluxed for 1 hour before bringing the pH to 10 using sodium hydroxide. Half of the solvent was removed by evaporation and the remaining solvent was allowed to slowly evaporate to give a solid that was recrystallised using methanol and water (10 : 1) to get needle-shaped colourless crystals of L. It was dried *in vacuo* over P_2O_5.Yield = 0.097 g, 40%, m.p. = 125°C, *m/z* = 244.

Synthesis of the complexes

The metal complexes $[ML_2(ClO_4)_2]\cdot 2H_2O$ (M = Ni or Cu) and $[MLX_2]nH_2O$ (M = Cu X = Cl or Br, n = 0; M = Ni, X = Cl, n = 3; M = Ni, X = Br, n = 0) were isolated by the following common procedure. An ethanol/THF solution (10 cm^3) of the metal salt (1 mmol) was mixed with (L) (2 mmol for the perchlorate complexes and 1 mmol for chloro- and bromo-complexes) and refluxed on a water bath for 1–2 hours, whereupon a solid precipitated. It was filtered, washed with ethanol/THF and dried in vacuo over P_2O_5.

Attempts to synthesise complexes with the composition $[ML_2X_2]$(X = Cl or Br) by mixing the metal salt and (L) in 1:2 mole ratio resulted only in the precipitation of $[MLX_2]$-type complexes.

CAUTION: Perchlorate salts with organic ligands can form potentially explosive mixtures. Necessary precaution should be taken during the preparation of the complexes. Only small amounts of the complex should be prepared and handled with care.

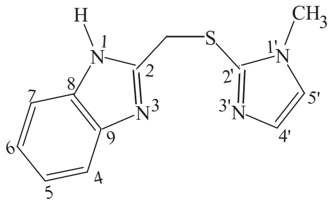

Fig. 1 2-(N-methylimidazole-2′-yl-thiomethyl)benzimidazole (L).

Physical measurements

Microanalyses were carried out on a Carlo-Erba analyser. Molar conductivity measurements at *ca* 10^{-3} M were made at room temperature using an Elico-82T conductivity bridge with a conventional dip-type conductivity cell. IR (as KBr pellets) and far-IR (in polyethylene powder) spectra of the compounds were recorded on Shimadzu IR-435 and Bruker IFS-113VFF spectrophotometers respectively. Thermogravimetric analyses were carried out using a Shimadzu DTA 40 analyser under dinitrogen. Solid state UV-Vis spectra were recorded in nujol mulls using a Hitachi 150-20 spectrophotometer. X-band ESR spectra of the copper complexes (in powder form) were recorded on a Varian E 109 spectrometer at room temperature using DPPH (g = 2.0036) as a standard. Room temperature magnetic moments were measured with a Gouy balance using $Hg[Co(CNS)_4]$ as the calibrant.

Results and discussion

(L) reacts with the metal salts in ethanol/THF at refluxing temperature according to equations (1) and (2) to afford the complexes of the formulae $[ML_2(ClO_4)_2]\cdot 2H_2O$ (M = Ni or Cu) and $[MLX_2]nH_2O$ (M = Cu, X = Cl or Br, n = 0; M = Ni, X = Cl, n = 3; M = Ni, X = Br, n = 0).

$$M(ClO_4)_2 + 2L + 2H_2O \rightarrow [ML_2(ClO_4)_2]\cdot 2H_2O \quad (1)$$

$$MX_2 + L + nH_2O \rightarrow [MLX_2]nH_2O \quad (2)$$

The analytical data (Table 1) of the complexes conform to the proposed formulae. Molar conductance values indicate the 1 : 2 electrolyte nature of perchlorate complexes in DMF. The chloro- and bromo-complexes showed non-electrolyte behaviour.

Thermal decomposition data

The thermogravimetric analysis of the copper(II) perchlorate complexes indicate the loss of two water molecules in the temperature range 110–130°C whereas that of the chloro-complex of nickel(II) showed loss of three molecules of water in the same range, thus confirming the lattice-held nature of these water molecules. The nickel(II) perchlorate complex exhibited loss of two water molecules in the range 150–170° suggesting their coordinated nature.

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Table 1 Physical and analytical data of the compounds

Compound	Colour	M.p./d.p./°C	λ_M /Ω^{-1}cm^{2}mol^{-1}	Analytical data/% Found (Calc.) C	H	N
L **(1)**	White	118	–	58.2 (58.9)	4.9 (4.9)	22.6 (22.9)
$[NiL_2(H_2O)_2](ClO_4)_2$**(2)**	Green	245^a	156	36.2 (36.8)	3.1 (3.6)	13.5 (14.3)
$[CuL_2(OClO_3)_2]2H_2O$**(3)**	Brown	235	135	36.5 (36.6)	3.1 (3.5)	14.1 (14.2)
$[NiLCl_2]3H_2O$**(4)**	Blue	235	59	33.7 (33.7)	3.9 (4.2)	12.6 (13.1)
$[CuLCl_2]$**(5)**	Green	210	20	37.9 (38.0)	3.2 (3.2)	14.5 (14.8)
$[NiLBr_2]$**(6)**	Blue	201	28	30.8 (31.1)	2.5 (2.6)	11.7 (12.1)
$[CuLBr_2]$**(7)**	Brown	195	13	31.6 (30.8)	2.4 (2.6)	11.2 (11.9)

Molar conductance values of *ca* 10^{-3}M solutions in DMF around 25°C.
d.p., Decomposition points.

IR spectra

The IR spectra of (L) and its complexes have been recorded as KBr disks. The ligand exibits a band around 3390 cm^{-1} due to the ν(NH) of the benzimidazole ring, a band around 1635 cm^{-1} assignable to ν(C=C) and ν(C=N) and another band around 1400 cm^{-1} characteristic of the $N–CH_3$ deformation vibration. The IR spectra of the complexes are comparable to those of the uncoordinated N-heterocycle except for minor shifts in the position of the bands. The ν(N–H) band shifts to lower frequency by about 200 cm^{-1} whereas ν(C=C)/ν(C=N) register about 5–10 cm^{-1} shift in the complexes. The perchlorate complexes, in addition to ligand bands, show characteristic peaks due to perchlorate ion around 1100 (ν_3) and 620 cm^{-1} (ν_4). In the case of the copper(II) perchlorate complex the ν_3 band is split, indicating the monodentate coordination of perchlorate, whereas in the spectra of the nickel(II) perchlorate complex, the perchlorate bands are characteristic of ionic perchlorate.[2,3] Nevertheless, the perchlorate complexes showed 1 : 2 electrolyte behaviour in DMF and this can be attributed to the displacement of the coordinated perchlorate ion by a solvent molecule. The absorption due to O–H stretching of the lattice water occurs around 3500 cm^{-1} and that of the coordinated water around 3350 cm^{-1}. The far-IR spectra of the chloro- and bromo-complexes, recorded as polyethylene pellets, exhibit bands assignable to metal-halogen stretching at 291 cm^{-1} (ν_{Ni-Cl}), 306 cm^{-1}(ν_{Cu-Cl}), 232 cm^{-1}(ν_{Ni-Br}) and 258 cm^{-1}(ν_{Cu-Br}), indicating the coordination of halide to the metal ion.[4,5,6] The chloro-complex of copper(II) also showed a band at 225 cm^{-1} due to the chloride bridge between the copper centres.

ESR data

The X-band ESR spectra of powdered samples of the copper(II) complexes were recorded at room temperature. The complexes exhibit a broad ESR signal without any hyperfine structure. Apparently the solids are not sufficiently magnetically dilute to yield well-resolved spectra at room temperature.[7] The $<g_{av}>$ data obtained for the complexes are 2.15, 2.16 and 2.07 respectively for chloro-, bromo- and perchlorate-complexes. In addition, the chloro-complex exhibits a weak signal around g = 4.3 corresponding to a spin forbidden half-field ($\Delta M_S = 2$) transition. An ESR signal around g ~ 4 in copper(II) complexes is diagnostic of their dimeric nature.[8] A slightly higher magnetic moment (2.23 BM) observed in the case of the chloro-complex of copper(II) could be attributed to ferromagnetic interaction.[9]

Electronic spectra

Electronic spectral data of the ligand and the complexes in the solid state are reported in Table 3. In the spectrum of the ligand

Table 2 Selected IR bands (cm^{-1}) of the ligand and its complexes

Compound	$\nu_{O-H}(H_2O)$	$\nu_{N–H}$	$\nu_{C=N}$	ν_{M-X}	$\nu_3(ClO_4)$	$\nu_4(ClO_4)$
1	–	3395 m	1636 w	–	–	–
2	3364 m	3152 m	1631 w	–	1109 s	633 m
3	3447 m	3141 m	1630 w	–	1124 s,1109 s	622 m
4	3500 b	–	1625 w	291 m	–	–
5	–	3229 m	1631 w	306 m, 225 w	–	–
6	–	3121 m	1626 w	232 m	–	–
7	–	3225 m	1631 w	258 m	–	–

Spectra recorded in KBr discs. For the far-IR range polyethylene disks were used.
S, strong; m, medium; b, broad; w, weak.

Table 3 Magnetic moment and electronic spectral data of the compounds

Compound	μ_{eff}/BM	λ_{max}/cm^{-1}
1		36 100, 35 000,
2	3.18	36 360, 35 100, 24 390, 15 040
3	1.76	36 760, 35 970, 27 770, 23 100, 12 630
4	3.68	36 360, 35 710, 17 860, 10 000, 7550
5	2.30	36 300, 27 340, 24 390, 15 980
6	3.40	35 970, 35 080, 17 391, 10 000, 7692
7	1.78	36 630, 35 720, 26 800, 25 080, 21 900, 11 790

Electronic spectra recorded in Nujol mulls.

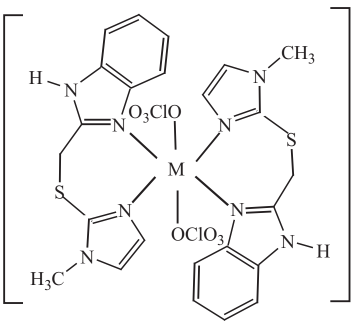
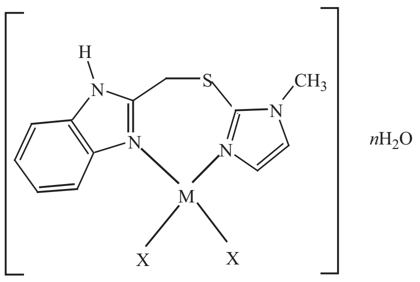


Fig. 2 Proposed structure of perchlorate complex of Cu(II).



M = Ni, X = Cl, *n* = 3; M = Ni, X = Br, *n* = 0; M= Cu, X=Br, *n*=0).

Fig. 4 Proposed structure of chloro-and bromo-complexes.

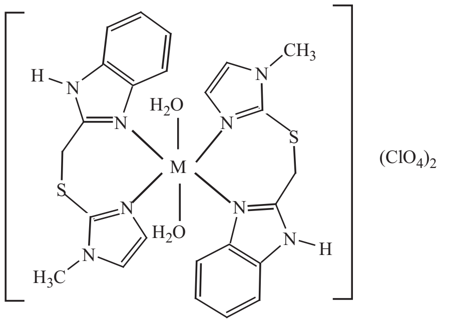


Fig. 3 Proposed structure of perchlorate complex of Ni(II).

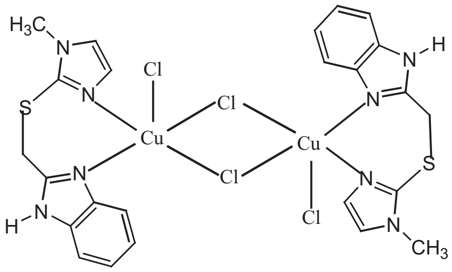


Fig. 5 Proposed structure of chloro-complex of Cu(II).

two bands are displayed around 36 300 and 35 000 cm^{-1} in the UV range. They are ascribed to the $\pi \rightarrow \pi^*$ transitions of the ligand. In the complexes, these bands are slightly shifted to higher wavenumber. The green coloured perchlorate complex of nickel(II) exhibits absorption bands centred at 15 000 and 24 300 cm^{-1}. They are assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$, respectively, of octahedral geometry (Fig. 3).[10] The chloro-and bromo-complexes of nickel(II) exhibit similar spectra, with three bands in the regions 7500, 10 000 and 17 500 cm^{-1}. They are assigned to the transitions $^3T_1(F) \rightarrow {}^3T_2(F)(\nu_1)$, $^3T_1(F) \rightarrow {}^3A_2(\nu_2)$ and $^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3) of tetrahedral geometry (Fig. 4).[11] The electronic spectrum of the copper(II) perchlorate complex displays a broad band around 12 600 cm^{-1}due to a d-d transition and a shoulder around 24 000 cm^{-1} arising from a $\pi(N) \rightarrow Cu$ charge transfer transition.[12,13] An octahedral geometry (Fig. 2) around the metal ion has been proposed to the complex based on the electronic and ESR spectral data. The chloro-complex of copper(II) exhibits absorption bands around 13 000 (d–d) and 24 400 cm^{-1} $\{\pi(N)\rightarrow Cu)\}$. Furthermore, the ESR spectrum of the chloro-complex displays a weak half-field signal around $g = 4.2$, indicating the dimeric nature of the complex. A typical axial ESR spectrum with $g = 2.1$ for this complex was observed. These results suggest a square pyramidal geometry (Fig. 5) around the copper ion. The bromo complex of copper(II) showed bands around 12 000 (d–d) and 22 000 cm^{-1} (Br→Cu), transitions characteristic of tetrahedral geometry (Fig. 4) around copper. The absence of a strong band around 30 000 cm^{-1} assignable to $\sigma(S) \rightarrow Cu$ in the spectra of copper complexes indicates the non involvement of sufur in the coordination.[14]

On the basis of conductivity, IR and electronic spectral studies discussed above an octahedral geometry to perchlorate complexes, we propose tetrahedral geometry to the chloro- and bromo-complexes of nickel(II) and the bromo-complex of copper(II), and a square pyramidal geometry to the chloro-complex of copper(II). The ligand shows bidentate nature coordinating *via* the tertiary nitrogens of imidazole and benzimidazole. Sulfur, although a potential coordinating atom, does not appear to participate in coordination in the complexes under study.

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