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Coordination Behaviour of Herbicidal Schiff Bases Derived from 2-Amino-6-Ethoxybenzothiazole towards Copper (II)

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The copper (II) chloride complex of 2-N-(salicylaldimine)-6-ethoxybenzothiazole (L_1), 2-N-(2′-hydroxy-3′-methoxybenzaldimine)-6-ethoxybenzothiazole (L_2), 2-N-(2′-hydroxy-1′-napthaldimine)-6-ethoxybenzothiazole (L_3), 2-N-(2′-furancarboxaldimine)-6-ethoxybenzothiazole (L_4), and 2-N-(2′-thiophenecarboxaldimine)-6-ethoxybenzothiazole (L_5) have the stoichiometry $[Cu(L_1)(H_2O)]Cl_2$, $[Cu(L_2)_2(H_2O)_2]Cl_3$, $[Cu(L_3)(H_2O)]Cl_2$, $[Cu(L_4)_2]Cl_2 \cdot 2H_2O$ and $[Cu(L_5)_2]Cl_2 \cdot 2H_2O$, respectively. The complex compounds have been isolated and characterised by elemental analysis, electrical conductivity, magnetic measurements, and infrared spectral measurements.

INTRODUCTION

The coordination chemistry of the Schiff bases derived from mixed heterocyclic amines is quite interesting. We have, therefore, studied the coordination behaviour of Schiff bases derived from 2-amino-6-ethoxybenzothiazole and salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, 2-furancarboxaldehyde, or 2-thiophenecarboxaldehyde towards copper (II).

EXPERIMENTAL

2-Hydroxy-3-methoxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, 2-thiophenecarboxaldehyde (Fluka), pure grade, and salicylaldehyde (Sarabhai M. Chemicals), were used as such. 2-Furancarboxaldehyde (Koch Light) was freshly distilled at 144°C before use. 2-Amino-6-ethoxybenzothiazole (Koch Light), practical grade, was recrystallized from dry ethanol, and dried over fused calcium chloride. Hydrated copper (II)-chloride (BDH) was dehydrated at 120°C.

10 mmol of 6-ethoxy-2-aminobenzothiazole was dissolved in *ca.* 50 cm^3 dry ethanol. The ethanol solution of aldehyde (10 mmol) was added to it with continuous mechanical stirring. The contents were refluxed for 1 hr. The solid compound thus formed, was cooled, filtered under suction, recrystallized from acetone and dried under IR lamp.

2-N-(Salicylaldimine)-6-ethoxybenzothiazole (L_1) (yellow colour, yield 90%, m.pt 126°C), 2-N-(2′-hydroxy-3′-methoxybenzaldimine)-6-ethoxy-

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benzothiazole (L_2) (orange, yield 76% m.pt. 149°C), 2-N-(2′-hydroxy-1′-naphthaldimine)-6-ethoxybenzothiazole (L_3) (orange, yield 72%, m.pt. 183°C), 2-N-(2′-furancarboxaldimine)-6-ethoxybenzothiazole (L_4) (yellow, yield 74%, m.pt 135°C), and 2-N-(2′-thiophenecarboxaldimine)-6-ethoxybenzothiazole (L_5) (yellow, yield 75%, m.pt 161°C) were prepared by similar method.

All the complexes were prepared by following general method. An acetone solution of 0.1345 g (1 mmol) anhydrous copper (II)chloride was added to the ligand in required molar ratio dissolved in acetone. The contents were reacted at room temperature (35°C). The required complexes, thus formed, were cooled, filtered under suction and washed with water, benzene and ether. The complex was recrystallized from acetone, and dried under IR lamp (yield *ca.* 72–85%).

RESULTS AND DISCUSSION

All the compounds are isolated in solid form have the composition $[Cu(L_1)(H_2O)]Cl_2$, $[Cu(L_2)_2(H_2O)]Cl_2$, $[Cu(L_3)(H_2O)]Cl_2$, $[Cu(L_4)_2]Cl_2 \cdot 2H_2O$ and $[Cu(L_5)_2]Cl_2 \cdot 2H_2O$. All the complexes behave as 1 : 2 electrolytes in methanol or acetone (250–260 ohm^{-1} $mole^{-1}$ cm^2), which indicates that both chloride ions are uncoordinated. The magnetic moments of the complexes are in the range of 1.61 to 1.91 B.M., corresponding to one unpaired electron and Cu^{2+} oxidisation state. The elemental analyses and conductivity data suggest a probable 4-coordinate structure for these complexes. All compounds are soluble in methanol, ethanol and acetone but insoluble in hexane and water.

L_3 and L_4 are herbicidal Schiff bases. L_3 shows inhibition of germination against Chenopodium album (100%), Avena fatua (100%), Abutilon theophrasti (60%), Brassica kaber (30%) and Ipomoea purpurea (20%) in pre-emergence application. L_4 exhibits growth inhibition followed by necrosis from leaf margins after a few days (chlorosis eg. phenylureas, triazines) against Ipomoea purpurea (60%) and Chenopodium album (10%) in post-emergence application. L_4 also corresponds inhibition of germination against Avena fatua (100%) and Abutilon theophrasti (80%) in pre-emergence application. It has been noted that metal ions promote and assist the biological activity[1,2].

The main infrared peaks of Schiff bases and complexes are summarised in Table 1.

Dichloro (aquo)[2-N-(salicylaldimine)-6-ethoxybenzothiazole] copper (II)

2-Amino-6-ethoxybenzothiazole exhibits N-H asymmetric and symmetric stretching modes at 3400 cm^{-1} and 3270 cm^{-1} respectively. The strong bands at 1625 cm^{-1} and 1335 cm^{-1} are assigned as δNH_2 and $\nu C{=}NH_2$ vibrations respectively. The ring vibration corresponding to

TABLE 1

ASSIGNMENT OF MAIN INFRARED BANDS (cm^{-1}) OF SCHIFF BASES DERIVED FROM 2-AMINO-6-ETHOXYBENZOTHIAZOLE AND ITS COPPER (II) COMPLEXES

Assignment→ Compounds ↓	νOH (H_2O) (phenolic)	νCH=N (azomethine)	νC=N (ring)	Other bands
6-OEt-2ABT	3400 s, sp 3270 s, br	—	1525 s, sl. br	1625 (δNH_2) s, sp 1335 ($\nu C\text{-}NH_2$) s, sp
L_1	3390 w, sl. br	1585 vs, sp	1520 ms, sl, br	—
$[Cu(L_1)(H_2O)]Cl_2$	3300–3100 s, v. br	1605 s, sl. br	1520 ms, sp	520 (νM–O) 420 (νM–N) 390 (νM–S) mw, br
L_2	3400–3200 w, br	1590 s, sp	1560 ms, sp	—
$[Cu(L_2)_2(H_2O)_2]Cl_2$	3500–3200 vs, v. br	1590 s, sp	1560 ms, sp	505 (νM–O) 375 (νM–S) w, sl. br
L_3	3480–3340 w, br	1600 s, sp	1570 ms, sp	—
$[Cu(L_3)(H_2O)]Cl_2$	3500–3200 ms, v. br	1625 s, sl. br	1570 ms, sp	510 (νM–O) 420 (νM–N) 395 (νM–S) w, br
L_4	—	1595 vs, sp	1540 m, sp	—
$[Cu(L_4)_2[Cl_2 \cdot 2H_2O$	3400–3200 m, v. br	1600 s, sl. br	1540 m, br	510 (νM–O) 420 (νM–N) w, br
L_5	—	1615, 1590 s, sp (doublet)	1520 s, sp	—
$[Cu(L_5)_2]Cl_2 \cdot 2H_2O$	3450–3100 w, br	1590 vs, sp	1520 m, sp	425 (νM–N) 365 (νM–S) w, br

benzothiazole νC=N (ring) shows at 1525 cm^{-1}. The νC–S vibration appears at 630 cm^{-1}. A very strong sharp band at 2965 cm^{-1} and strong, broad (slightly) band at 2920 cm^{-1} are assigned νCH_3 and νCH_2 vibrations. Infrared spectrum of 2-N-(salicylaldimine)-6-ethoxybenzothiazole shows a weak, slightly broad band at 3390 cm^{-1}, which is assigned to the phenolic hydroxy group. A very strong band at 1585 cm^{-1} is assigned as νCH=N (azomethine), and medium strong band at 1535–1520 cm^{-1} is assigned as νC=N (ring) vibrations. The strong sharp band at 1245 cm^{-1} is attributed to the νC–OH vibrations and strong sharp band at 785 cm^{-1}, 770 cm^{-1}, 750 cm^{-1} and 725 cm^{-1} are assigned as *o*-disubstituted benzene ring vibrations[3]. νC–S band appears at 600 cm^{-1}.[3]

In the spectrum of the complex, strong and broad band appeared at 3300 cm^{-1} and 3100 cm^{-1}. The greatly increased intensity and broad nature of these bands indicate presence of hydroxy group, and water molecule within the complex. In 1600 cm^{-1} to 1400 cm^{-1} region, strong, sharp bands of the ligand modified and shifted to higher frequency region. Azomethine bands appear at 1605 cm^{-1}, 1590 cm^{-1} and show 10–25 cm^{-1} positive shift on complexation. νC=N (ring) band appears at 1520 cm^{-1}, which is unaffected on complexation. νC–OH vibrational band appears at 1260 cm^{-1} with 15 cm^{-1} positive shift. This may be interpreted as due to the coordination of unionised phenolic group.[4,5] Characteristic vibrations of *o*-disubstiuted benzene ring also suffer 10–25 cm^{-1} positive shift and appear at 810 cm^{-1}, 780 cm^{-1}, 760 cm^{-1}, and 735 cm^{-1}. The νC–S band appears at 610 cm^{-1} with 10 cm^{-1} positive shift. New medium weak and broad bands at 520 cm^{-1}, 420 cm^{-1}, and 390 cm^{-1} may correspond to the νM–O, νM–N, and νM–S respectively.[6] Shifting of azomethine band in 1600 cm^{-1} region, and appearance of new bands in 500–300 cm^{-1} region indicate coordination of ligand with metal. The Schiff base acts as a tridentate ligand (ONS) through phenolic oxygen, azomethine nitrogen, and ring sulphur.

Dichloro(diaquo)-bis-[2-N-(2′-hydroxy-3′-methoxybenzaldimine)-6-ethoxybenzothiazole]copper (II)

2-N-(2′-hydroxy-3′-methoxybenzaldimine)-6-ethoxybenzothiazole exhibits a weak, very broad envelope around 3400–3200 cm^{-1} probably due to the hydroxy group. A strong sharp band at 1590 cm^{-1} is assigned as νCH=N (azomethine), vibration, and νC=N (ring) vibrational bands are observed at 1560 cm^{-1} and 1550 cm^{-1}. The strong sharp bands at 1440 cm^{-1} and 1250 cm^{-1} correspond to the νC–OCH$_3$ and νC–OH vibrations, respectively. Skeletal vibrations of 1,2,3-trisubstituted benzene ring appear at 780 cm^{-1}, 735 cm^{-1} and 720 cm^{-1}. The νC–S band appears at 600 cm^{-1}. In the spectrum of the complex, a very strong and very broad band centred at 3350 cm^{-1} (3500–3200 cm^{-1}) is assigned as νOH vibrations of the hydroxyl group and coordinated water molecules. νCH=N (azomethine), νC=N (ring), νC–OCH$_3$, and νC–OH bands remain unchanged on complexation. Other skeletal vibrations trisubstituted benzene ring (700 cm^{-1} region) are almost unaffected. But the νC–S band shifts to 620 cm^{-1} with 20 cm^{-1} positive shift, indicating coordination through the ring sulphur atom. The absence of any change in these bands suggests that the azomethine group is not involved in coordination, and the phenolic part is also not affected in the complex. New weak and slightly broad band appear at 505 cm^{-1} and 375 cm^{-1} which may be attributed to the ν(M–O)(H_2O), and ν(M–S) vibrations respectively.[6]

It is interesting to note that the Schiff base has only one additional group (3-methoxy) compared to the Schiff base derived from salicylaldehyde but this acts as a monodentate ligand while salicylaldimine acts a tridentate ligand (ONS). This Schiff base coordinates through ring sulphur only. This may be attributed to the steric effects of the methoxy group.

Dichloro(aquo)-[2-N-(2′-hydroxy-1′-naphthaldimine)-6-ethoxybenzothiazole]Copper (II)

In the spectrum of Schiff base, there is a weak and broad envelop around 3480–3340 cm^{-1} assigned to hydroxyl group vibration. A strong, sharp band at 1600 cm^{-1} is assigned to the ν(CH=N) (azomethine), and medium strong band at 1570 cm^{-1} is assigned as ν(C=N) of benzothiazole ring. Medium sharp bands at 1618 cm^{-1}, 1490 cm^{-1} are assigned *o*-disubtiuted napthalene ring stretching vibrations and medium sharp bands at 750 cm^{-1}, 740 cm^{-1} and 730 cm^{-1} are characteristic vibrations due to the 4-adjacent hydrogen in naphthalene ring.[3] A medium strong, sharp band at 1260 cm^{-1} is attributed to the νC–OH vibration, and νC–S band appears at 620 cm^{-1}. Infrared spectrum of the complex exhibits the greatly increased intensity and broad nature of the bands centred at 3350 cm^{-1} (3500 cm^{-1} to 3200 cm^{-1}), which corresponds to the hydroxyl group, and water molecule coordinated to the complex. The νCH=N band of the ligand shifts to 1625 cm^{-1} with a shoulder at 1590 cm^{-1}. νC=N (ring) band is unchanged on complexation and appears at 1570 cm^{-1}. *o*⁻-Disubstituted naphthalene ring bands in 1600 cm^{-1} region are merged in azomethine band and the other skeletal band at 1490 cm^{-1} is unaffected. νC–OH vibrational band appears at 1270 cm^{-1} with 10 cm^{-1} positive shift. This may be interpreted as due to the coordination of unionized phenolic group.[4,5] νC–S band appears at 625 cm^{-1} with 5 cm^{-1} positive shift. New weak and slightly broad bands at 510 cm^{-1}, 420 cm^{-1} and 395 cm^{-1} may be attributed to the ν(M–O), ν(M–N) and ν(M–S) vibrations respectively.[6] Shifting of azomethine, ν(C–OH_2) and ν(C–S) band indicate coordination through azomethine nitrogen, phenolic oxygen and ring sulphur. Appearance of ν(M–O), ν(M–N) and ν(M–S) bands also support coordination and tridentate nature of this ligand through (ONS) donor set.

Dichchloro-bis-[2-N-(2′-furancarboxaldimine)-6-ethoxybenzothiazole] copper (II) dihydrate:

Spectrum of 2-N-(2′-furancarboxaldimine)-6-ethoxybenzothiazole shows a very strong, sharp band at 1595 cm^{-1} which is assigned as νCH=N (azomethine) and a medium, sharp band at 1540 cm^{-1} assigned as νC=N (ring). Very strong sharp bands at 1575 cm^{-1}, 1400 cm^{-1} and a broad band at 1475 cm^{-1} (1490–1460 cm^{-1}) can be assigned as 2-substituted furan ring vibrations[3]. The strong sharp bands at 775 cm^{-1} and 720 cm^{-1} are characteristic C—H wagging modes of furan ring. νC—S band appears at 615 cm^{-1}. Spectrum of the complex exhibits medium and very broad band at 3300 cm^{-1} (3400–3200 em^{-1}) correspond to the uncoordinated water molecules. Azomethine band appears slightly shifted at 1600 cm^{-1} but νC=N (ring), ν(C—S) bands are unaffected on coordination and appear at 1540 cm^{-1} and 615 cm^{-1} respectively. Furan ring vibrational bands show 5–10 cm^{-1} shift and appear at 1585 cm^{-1}, 1485 cm^{-1}, 1405 cm^{-1}, and a doublet at 1450, 1440 cm^{-1}. New weak and slightly broad bands appeared at 510 cm^{-1} and 420 cm^{-1} which may be correspond to the ν(M–O) (furan ring) and ν(M–N) modes of vibrations respectively. Shifting of azomethine and furan ring vibrational bands indicate coordination through azomethine nitrogen and oxygen of furan ring. This is also supported by ν(M–N) and ν(M–O) bands. Thus this Schiff base acts as a bidentate ligand utilizing the (NO) donor set.

Dichloro-bis-[2-N(2′-thiophenecarboxaldimine)-6-ethoxybenzothiazole] copper (II) dihydrate

Spectrum of Schiff base shows a strong doublet at 1615, 1590 cm^{-1} corresponding to the νCH=N (azomethine) and a medium strong sharp band at 1520 cm^{-1} assigned as νC=N (ring). Strong and sharp bands at 1390 cm^{-1}, 1360 cm^{-1} and a strong broad band at 1430 cm^{-1} are assigned as 2-substituded thiophene ring vibrational bands[3]. Strong sharp bands in 800–700 cm^{-1} region are assigned CH wagging modes. ν(C–S) band of benzothiazole ring appears at 620 cm^{-1}. Infrared spectrum of the complex exhibits a medium weak and very broad band at 3350 cm^{-1} (3450–3100 cm^{-1}) corresponding to the presence of water molecules in the complex. Azomethine band shows 15–25 cm^{-1} negative shift and appears at 1590 cm^{-1} and 1575 cm^{-1}. νC=N (ring), and ν(C–S) (benzothiazole ring) bands remain almost unchanged and appear at 1520 cm^{-1} and 620 cm^{-1}, respectively. 2-Substituted thiophene ring vibrational bands appear at 1475 cm^{-1} 1445 cm^{-1} and 1395 cm^{-1} with 5–15 cm^{-1} shift. In 500–300 cm^{-1} region, new medium weak and sharp bands appear at 425 cm^{-1} and 365 cm^{-1}, which may be attributed to ν(M–N) and ν(M–S) (thiophene ring) vibrations respectively. Shifting of azomethine, thiophene ring bands and appearance of ν(M–N) and ν(M–S) bands indicate coordination of ligand through azomethine nitrogen and thiophene ring sulphur. Thus this Schiff base acts as bidentate ligand with (NS) donor set.

Schiff bases derived from 3-amino-6-ethoxybenzothiazole can act as bidentate ligand through ring sulphur or ring nitrogen, and azomethine nitrogen but functional groups suitably placed in aldehydes can provide additional donor sites.

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