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# Copper(II) Complexes of 4-Azocyanoacetamidoaniline Antipyrine and 4-Azocyanoacetamido-*m*-toludine Antipyrine

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The synthesis and characterization of copper(II) complexes with 4-azocyanoacetamido-aniline antipyrine ($HL^1$) and 4-azocyanoacetamido-m-toludine antipyrine ($HL^2$) are reported. Elemental analyses, molar conductivities, magnetic moments and spectral (IR, electronic and ESR) studies have been used. The elemental analyses and IR spectra show that the ligands behave as neutral or monobasic bidentate ones, either in the ketoazo or enolazo form. The IR spectra also show that, in the chlorocomplexes (1 and 4), the cyano group is changed to amide (—CO—$NH_2$). Stereochemical structures for the complexes are proposed.

**Key words:** complexes, IR, ESR spectra, magnetic properties, conductivity, synthesis

Antipyrine (2,3-dimethyl-1-phenyl-5-pyrazolone) and its derivatives exhibit a wide variety of potentially useful applications including biological [1], clinical [2], and pharmacological [3,4]. Antipyrines have also been used as analytical reagents in the estimation of some metal ions [5,9]. Considerable study of Schiff bases and azo containing compounds derived from 4-aminoantipyrine and 4-formylantipyrine has been reported [10]. For this paper, copper(II) complexes of 4-azocyanoacetamidoaniline antipyrine ($HL^1$) and 4-azocyanoacetamido-m-toludine antipyrine ($HL^2$) have been prepared and characterized.

## EXPERIMENTAL

Reagent grade chemicals were used without further purification. The ligand 4-azocyanoacetamidoaniline antipyrine and 4-azocyanoacetamido-m-toludine antipyrine were prepared by coupling the diazonium salt of aniline, m-toludine with cyanoacetamido antipyrine in pyridine. The product was recrystallized several times from ethanol. The copper complexes were prepared by heating under reflux on water bath for *ca*. 24 hrs, 0.002 moles of copper salt with 0.002, 0.004 or 0.001 moles of 4-azocyanoacetamidoaniline antipyrine and 4-azocyanoacetamido-m-toludine in *ca*. 50 ml EtOH in the presence of an appropriate amount of AcONa. The resulting solids were filtered off, washed several times with EtOH and dried under vacuum over $P_4O_{10}$. The reactions of the ligands with Ni(II) and Co(II) salts gave complexes difficult to separate as solids or difficult to characterize. Elemental analyses (C, H, Cl) were per-

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formed and copper analysis were carried out by standard method [11]. IR spectra were performed as KBr discs, using a Perkin-Elmer 1430 recording spectrophotometer. $^1$H NMR spectrum was recorded in d$^6$-DMSO using a 300 MHz Varian NMR spectrometer. The electronic spectra were carried out in N,N-dimethylformamide (DMF) solution using a Perkin-Elmer lambda 4B spectrophotometer. The molar conductivity measurements (Table 1) were made in DMF solutions ($10^{-3}$ M) using a Tacussel conductometer. Magnetic susceptibilities were measured at 27°C by the modified Gouy method. The magnetic moments were calculated from $\mu_{eff} = 2.84\sqrt{X_M^{corr}T}$. ESR spectra were recorded with a Varian E104 spectrometer and calibrated with diphenyl picrylhydrazide.

## RESULTS AND DISCUSSION

The ligands ($HL^1$ and $HL^2$) were prepared and characterized by elemental analyses, infrared (Table 2) and $^1$H NMR spectroscopy. The infrared spectra show bands at 3395–3380, 3180–3165, 2210–2205, 1680, 1655–1645,1610–1585 and 1545 cm$^{-1}$. The first two bands are assigned to ν(N-H) groups and the other bands are assigned to ν(C≡N), ν(C=O) (amide I), ν(C=O) of pyrazolone ring, ν(C=N) and ν(N=N) respectively. The $^1$H NMR spectra of the ligands have been recorded in d$^6$-DMSO at room temperature. The spectra confirm their structures and show strong signals at δ = 2.0–2.2 (3H) and δ = 2.9–3.0 (3H), due to C-$CH_3$ and N-$CH_3$ protons respectively. Resonances at (9.4–9.1) and (11.8–11.7) ppm were assigned to Ar-NH- and -NH-CO- respectively. The down field shift of the -NH-CO- signal can be attributed to intermolecular hydrogen bonding to the solvent. The elemental analyses, infrared and $^1$H NMR data are compatible with the structure shown in Fig. 1.

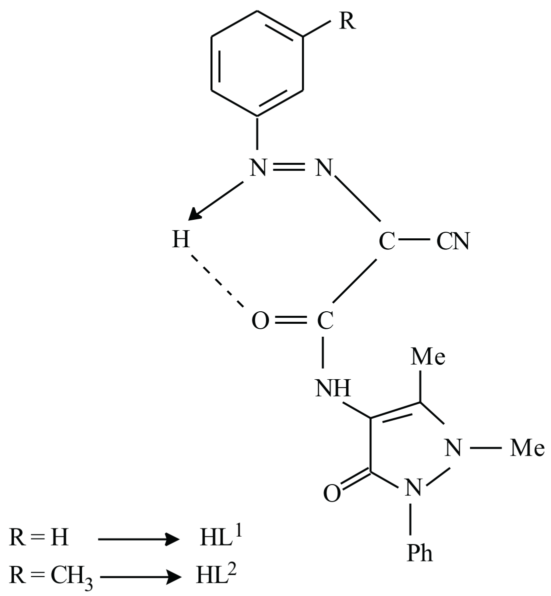



**Figure 1.** The structure of used ligands.

**Table 1.** Colors, molar conductivities and magnetic properties of 4-azocyanoacetamidoaniline antipyrine, ($HL^1$), and 4-azocyanoacetamido-m-toludine antipyrine ($HL^2$) and their copper complexes.

| No. | Compound | Color | $\Lambda_M$(ohm$^{-1}$ cm$^2$ mol$^{-1}$) | $\mu_{eff}$ (B.M) per $Cu^{2+}$ ion |
|---|---|---|---|---|
| | $HL^1$ | yellow | – | – |
| 1 | $[CuL^1Cl_2(H_2O)_2]\cdot H_2O$ | green | 75.0 | 1.65 |
| 2 | $[Cu_2L^1_2(OH)_2]$ | green | 40.0 | 0.96 |
| 3 | $[CuL^1(ClO_4)(H_2O)]$ | brown | 38.0 | 1.8 |
| | $HL^2$ | yellow | – | – |
| 4 | $[Cu_2L^2Cl_4]\cdot 2H_2O$ | green | 45.0 | 1.65 |
| 5 | $[Cu_2L_2(OH)_3(H_2O)]\cdot H_2O$ | green | 6.9 | 0.0 |
| 6 | $[Cu_2L^2_2(OH)_2(H_2O)_2]$ | green | 25.3 | 1.03 |
| 7 | $[CuL^2(ClO_4)(H_2O)]\cdot 3H_2O$ | green | 7.11 | 1.85 |

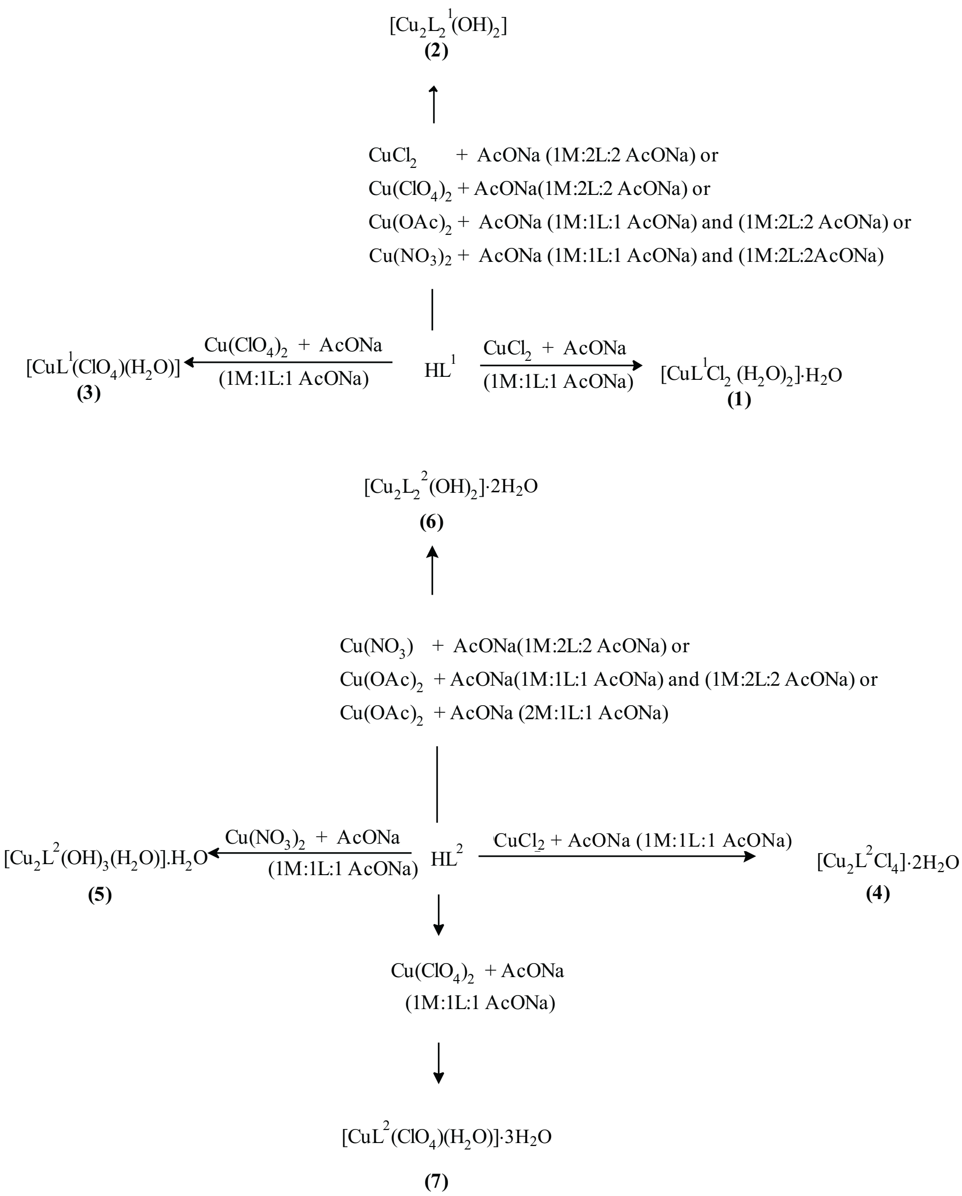
The analytical data show that the reactions of ligands ($HL^1$, $HL^2$) with different salts of Cu(II) ion in the presence of appropriate amounts of trihydrate sodium acetate give different types of complexes depending on the molar ratio and copper(II) salt as shown in Scheme 1.

These air stable complexes are non-hygroscopic, partially soluble in most organic solvents, but easily soluble in DMF and DMSO. The molar conductivities in DMF ($10^{-3}$ M) solution (Table 1) show that the complexes behave as non-electrolytes [13,14], indicating coordination of the anions. The high molar conductivities found for some complexes are due to partial displacement of the anions by DMF. Characteristic IR spectral bands, most useful for establishing the coordination modes of the ligands, are given in Table 2. The infrared spectra of metal complexes show that the band corresponding to ν(C=O) of pyrazolone ring appears at the same frequency as those of the free ligands (complexes 1, 3, 7) or shifts to lower frequency in the spectra of the remainder complexes. This indicates that the pyrazolone carbonyl group is coordinated in the latter ones, however, it is uncoordinated in the former ones. The infrared spectra of all complexes, except the chloro complexes (1, 4) show that the band characteristic to ν(C≡N) appears at the same frequency, compared to those of the ligands. This band disappears from the spectra of complexes (1, 4), and new two bands appear at 3440–3435 and 1660 $cm^{-1}$, assigned to ν($NH_2$) and ν(C=O) respectively. This may be taken as an evidence that the C≡N is changed to CO-$NH_2$ by promotion of water to the cyano group [15]. The infrared spectra of all complexes except (1, 4) show no bands due to ν(C=O) (amide I) but show two bands at 1610–1600 and 1575–1560 $cm^{-1}$. These bands are assigned to ν(C=C) and ν(N=N) respectively, indicating that the ligands in these complexes react in the enol-azo form and coordination takes place *via* the enolic oxygen and azo nitrogen atoms, whereas, in the spectra of chloro complexes, the ν(C=O) band shifts to lower frequency compared to those of free ligands. Moreover, the infrared spectra of these two complexes show two bands at 3230 and 1630–1585 $cm^{-1}$, assigned to ν(NH) and ν(C=N) respectively, indicating that the ligands react in the keto-hydrazo form and coordination takes place through the car-

**Table 2.** Infrared spectral bands for 4-azocyanoacetamidoaniline antipyrine ($HL^1$) and 4-azocyanoacetamido-m-toludine antipyrine and their Cu(II) complexes.

| No. | Compound | ν($H_2O$) | ν(OH) | ν(N–H) | ν(C≡N) | ν(C=O)[a] | ν(C=O)[b] | ν(C=N) | ν(N=N) | ν(Cu–O) | ν(Cu–N) | ν(Cu–Cl) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $HL^1$ | – | 2800 (br) | 3395(s), 3210, 3165 | 2205 (s) | 1680(s) | 1645(s) | 1585(s) | 1545(s) | – | – | – |
| 1 | $[CuL^1Cl_2(H_2O)_2]\cdot H_2O$ | 3435(br) | – | 3435[d](s), 3340(s), 3220(sh) | – | 1625(s) | 1645(s) | 1585(s) | – | 475(m) | 435(m) | 310(m) |
| 2 | $[Cu_2L^1_2(OH)_2]$ | – | 3660(s), 3430(s) | 3360(sh) | 2215(s) | – | 1575(s) | – | 1560(s) | 455(m) | 405(m) | – |
| 3 | $[CuL^1(ClO_4)(H_2O)]$ | 3400(br) | – | 3250(s) | 2210(s) | – | 1645(s) | 1600[c](s) | 1565(s) | 505(m) | 495(m) | – |
| | $HL^2$ | – | – | 3380, 3180 | 2210(s), 2255(sh) | 1680(s) | 1655(s) | 1610(s) | – | – | – | – |
| 4 | $[Cu_2L^2Cl_4]\cdot 2H_2O$ | 3440(br) | – | 3440[d] (s), 3340(m), 3230(m) | – | 1660(s) | 1640(s) | 1630(s) | – | 459(m) | 445(w) | 315(m) |
| 5 | $[Cu_2L^2(OH)_3(H_2O)]\cdot H_2O$ | 3430(br) | 3660(s), 3530(s) | 3350(s) | 2216(s) | – | 1575(s) | – | 1570(s) | 505(m) | 455(w) | – |
| 6 | $[Cu_2L^2_2(OH)_2(H_2O)_2]$ | 3420(br) | 3660(s), 3530(s) | 3355(s) | 2210(s) | – | 1575(s) | – | 1565(s) | 495(w) | 455(m) | – |
| 7 | $[CuL^2(ClO_4)(H_2O)]\cdot 3H_2O$ | 3430(br) | – | 3250(m) | 2210(s) | – | 1655(s) | 1610[c](s) | 1575(s) | 500(m) | 455(m) | – |

[a]ν(C=O) of amide; [b]ν(C=O) of pyrazolone ring; [c]ν(C=C); [d]ν($NH_2$).




**Scheme 1.** Schematic representation of the different chemical reactions of ligands and different copper(II) salts.

bonyl oxygen and NH group. The spectra of complexes 3 and 7 show a very strong split band ($\nu_3$) at 1110 and 1070 $cm^{-1}$ and a strong band at 630 $cm^{-1}$ ($\nu_4$), which are indicative of a monodentate coordinated perchlorate [16]. The infrared spectra of hydroxo complexes show one or two bands near 3660 and 3530 $cm^{-1}$, assigned to ν(Cu-OH) [17]. The infrared spectra of all complexes show two bands at 505–455 and 495–405 $cm^{-1}$, assigned to ν(Cu-O) [18] and ν(Cu-N) [18] respectively. The chloro complexes show an additional new band at 315–310 $cm^{-1}$, assigned to ν(Cu-Cl) [19]. The spectra of complexes, which contain water molecules, show a band at 3435–3400 $cm^{-1}$, assigned to ν(OH), indicating hydration water. The infrared spectra of complexes 1, 3 and 5–7 show additional two bands near 960 and 640 $cm^{-1}$, owing to $\rho_{rock}$ ($H_2O$) and $\rho_{wagg}$ ($H_2O$) respectively. The appearance of the latter two modes indicates coordinated water rather than hydrated water [20]. The above arguments indicate that the ligands behave as neutral or monobasic bidentate ligands and coordination occurs *via* the carbonyl or enolic oxygen atom and NH group or the azo nitrogen atom.

The copper(II) complexes, $[CuL^1Cl_2(H_2O)_2]\cdot H_2O$, $[CuL^1(ClO_4)(H_2O)]$, $[Cu_2L^2Cl_4]\cdot 2H_2O$ and $[CuL^2(ClO_4)(H_2O)]$ exhibit magnetic moments (Table 1) close to the spin-only value for unpaired spin (~ 1.73 B.M.) at room temperature. Since the magnetic susceptibility of the complexes were not determined below room temperature, nothing can be said about the presence or absence of magnetic exchange. The rest of copper(II) complexes exhibit much lower room temperature magnetic moments than that observed for normal copper(II) complexes. This low magnetic moment suggests strong antiferromagnetic interactions between copper(II) ions.

The electronic spectra of the copper(II) complexes $[CuL^1(ClO_4)(H_2O)]$, $[Cu_2L^2Cl_4]\cdot 2H_2O$ and $[CuL^2(ClO_4)(H_2O)]\cdot 3H_2O$ show bands near 14890 $cm^{-1}$ and 17260 $cm^{-1}$. These positions suggest a square planar stereochemistry for such complexes. In the present complexes the bands have its origin in d-d transitions, which can be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ in increasing sequence of energy. The electronic spectra for the rest of the copper(II) complexes exhibit a broad absorption band at *ca.*12700 $cm^{-1}$. Such spectra are characteristic for octahedral copper(II) complexes [21].

The powder ESR parameters of the copper(II) complexes at room and liquid nitrogen temperature are listed in Table 3. The spectra recorded at liquid nitrogen temperature (77 K) are very similar to the room temperature spectra, indicating no significant change in stereochemistry. The single isotropic feature for the solids $[Cu_2L^2(OH)_3(H_2O)]H_2O$ and $[CuL^2(ClO_4)(H_2O)]\cdot 3H_2O$ suggests a significant interaction between copper(II) centers. The powder ESR spectrum of $[Cu_2L^2Cl_4]\cdot 2H_2O$ has a rhombic distortion with $g_1 > g_2 > g_3 > 2$, indicative of a complex with a $d_{x^2-y^2}$ ground state [22]. The rhombic signal is probably a consequence of the bulkiness of the ligand. In such cases the g-values can be related by the expression $G = (g_{11} - 2)/(g_\perp - 2)$, assuming $g_\perp = g_{11}$ and $[(g_2 + g_3)/2 = g_\perp]$ [23]. G for the chloro complex is less than four (G = 3.84), indicating that exchange interaction between the copper(II) centers is considerable in the polycrystalline solid. Kivelson and Heiman [24] have suggested that the $g_{11}$ value in the Cu(II) complex can be used as a measure of covalent character of the metal–ligand bond. For the ionic environment $g_{11}$ is normally 2.3 or higher and for the covalent environment it is less than 2.3. Using this criterion, the data show considerable covalent character of the metal–ligand bond in the present complexes.

**Table 3.** ESR spectral parameters of the complexes.

| Complexes | Temp. | $g_{11}$ or $g_1$ | $g_2$ | $g_\perp$ or $g_3$ | $g_{av}$ or $g_{iso}$ |
|---|---|---|---|---|---|
| $[CuL^1Cl_2(H_2O)_2]\cdot H_2O$ | RT | | | | 2.043 |
| | 77K | | | | 2.047 |
| $[CuL_2^1(OH)_2]$ | RT | | | | 2.099 |
| | 77K | | | | 2.103 |
| $[CuL^1(ClO_4)(H_2O)]$ | RT | | | | 2.106 |
| | 77K | | | | 2.104 |
| $[Cu_2L^2Cl_4]\cdot 2H_2O$ | RT | 2.221 | 2.093 | 2.022 | 2.122 |
| | 77K | 2.232 | 2.079 | 2.026 | 2.119 |
| $[Cu_2L^2(OH)_3(H_2O)]H_2O$ | RT | | | | 2.104 |
| | 77K | | | | 2.172 |
| $[CuL^2(ClO_4)(H_2O)]\cdot 3H_2O$ | RT | | | | 2.083 |
| | 77K | | | | 2.080 |

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