Copper(II) Mixed Ligand Complex with an *N*-Alkylated Diamine and a New β-Diketonate

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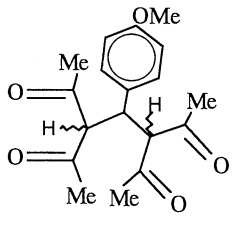
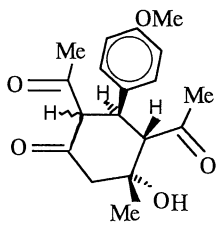
Reaction of two acetylacetones with *p*-anisaldehyde resulted in a new β-diketonate ligand which can form a mixed ligand Cu(II) complex with an *N*-alkylated ethylenediamine. The X-ray structure of the complex was determined and its chromotropic property in solution characterized .

In previous works, we could synthesize some solvatochromic dinuclear complexes using a tetraketonate ligand, i.e., 1,1,2,2-tetraacetylethanediide (taet).[1,2] In continuing these studies, we considered on a series of bis-β-diketonates of the type [acac$_2$CHR], such as H_2L^1, containing a spacer group between two acetylacetonate moieties, to synthesize bis-β-diketonato bridged binuclear mixed-ligand complexes of Cu(II). Bis-β-diketones of this type were originally synthesized by Shamma et al.,[3] and only a few reports have appeared on their metal-complexes.[4-6] Although the procedure for the synthesis of H_2L^1 was the same as Shamma method,[3] and elemental analysis data and IR absorption bands were same as reference, NMR studies led us to the structure of its isomer, HL^2. The X-ray analysis of its copper(II) mixed-ligand complex supported our assumption. In this communication, some properties of the new complex such as solvatochromic behaviour in solution and its crystal structure will be reported as well.

The ligand was prepared by mixing 0.50 mol of Hacac and 0.25 mol of *p*-anisaldehyde in 80 ml of EtOH (95%) and 50 drops of piperidine as the base catalyst. The mixture was allowed to stand at room temperature; a few days later, white crystals appeared which were recrystallized from benzene and MeOH. Elemental analysis : C% = 67.88 (67.90), H% = 6.53 (6.98); the values in parantheses are calculated ones. The FAB-MS spectrum also confirmed $C_{18}H_{22}O_5$ molecular formula for crystals , with M.W = 318.2. The infrared absorptions[7] were also similar to the reported data,[3] but its ^{1}H-NMR signals[8] were not in agreement with expected spectrum. With more investigation, using ^{13}C-NMR,[8] we assured that the reaction resulted in an isomer of H_2L^1 , i.e., HL^2 .



H_2L^1



HL^2

The copper(II) mixed-ligand complex was synthesized by mixing $CuCl_2 \cdot 2H_2O$, tmen, HL^2 and KOH with molar ratio 1:1:1:1 in EtOH. After filtration and reducing the volume of filtrate under low pressure, bluish-green crystals appeared which were recrystallized in dichloromethane(DCM). The elemental analysis data was in agreement with [CuCl($\mathbf{L^2}$)(tmen)]·DCM : C% = 48.87 (48.62), H% = 6.47 (6.70), N% = 4.70 (4.54) . Magnetic moment is μ_{eff} = 1.89 B.M. at room temperature.

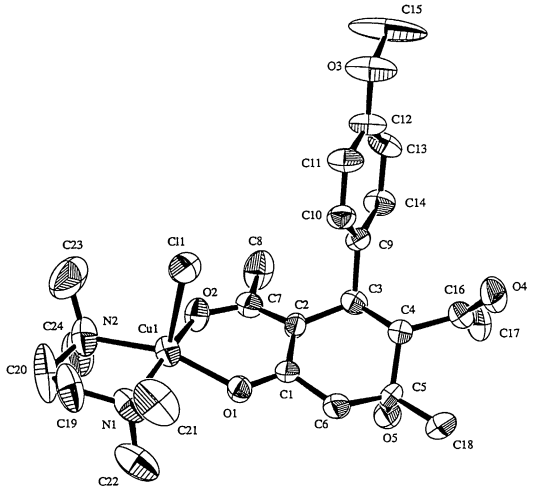


Figure 1. Molecular Structure of [CuCl($\mathbf{L^2}$)(tmen)].

Table 1. $\tilde{\nu}_{max}$ and ε_{max} values of [CuCl(L^2)(tmen)] in solid state and in various solvents[a] at room temperature

	$\tilde{\nu}_{max}$ (cm^{-1}) x 10^{-3}	ε_{max} (M^{-1}.cm^{-1})	Color
Solid[b]	15.81	—	bluish-green
MeOH	17.27	137.2	blue
EtOH	16.67	146.4	blue
DMSO	16.14	137.6	blue
DCE	14.45	170.0	green

a 0.01 M solution
b Solid reflectance spectrum shows a broad peak

FT-IR spectra show that C=O str. vibration which has two absorption bands in HL^2 at 1720 and 1693 cm^{-1} (related to two types of C=O bands) are shifted to 1587 and 1695 cm^{-1}, respectively, in copper complex. The first absorption band can be related to β-diketonate chelating moiety, and $\Delta\tilde{\nu}$ = -133 cm^{-1} indicates the extent of coordination of C=O to copper.[9]

The crystal structure of the complex was unambiguously determined by X-ray diffraction study,[10] which confirmed the relative stereochemistry of $\mathbf{L^2}$ depicted in the scheme. The ORTEP view is shown in Figure 1 . The Cu atom has a square-pyramidal coordination, where the two N atoms of tmen and the two O atoms of the β-diketonato moiety in $\mathbf{L^2}$ form the basal plane and the Cl atom occupies the apical site. The Cu atom is displaced 0.309 Å towards the Cl atom from the average basal plane. The Cu1-O1 and Cu1-O2 distances are almost the same

(192.5(4) and 192.6(4) pm, respectively).The bond length of Cu1-N1 (205.5(6) pm) and Cu1-N2 (207.2(5) pm) are also normal. The anisyl, acetyl, and methyl (C18) substituents on the six membered carbocycle of $\mathbf{L^2}$ occupy the pseudo-equatorial positions. The Cl atom of each complex molecule has a hydrogen bond to the OH group (O5) of $\mathbf{L^2}$ in a neighboring complex molecule (Cl...H, 2.15 Å ; Cl...H-O5, 167°).

The characteristic properties of this chelate are (1) its high solubility in various organic solvents and (2) the considerable change in color of solution from one solvent to another ; in other words, its solvatochromic property. All the spectral data obtained are summarized in Table 1.

Since the chloride anion as well as polar solvent molecules can be coordinated to the chelate cation , the competition of these two ligands for axial site(s) of the chelate cation happens. In a polar solvent, the chloride is attracted by positive ends of solvent molecules (hydrogen-bond is formed when solvent is amphiprotic). The Cu-Cl bond is weakend by this interaction, and finally dissociates off the chloride anion. As a 5-coordinate species in non-polar solvents such as dichloroethane(DCE), the color is green, and as a square-planar molecule in polar solvents such as MeOH, the color is blue. (In present case, similar weak hydrogen-bond O-H...Cl exists in solid state, and the color is bluish-green.)

The main driving force to dissociate the chloride anion from cation complex is anion solvation power of the used solvent, i.e, the *acceptor number* (AN).[11] With decreasing of solvent acceptor properties, $\tilde{\nu}_{max}$ values decrease : MeOH >EtOH >DMSO >DCE

The equilibrium of the dissociation and formation of the 5-coordinate complex is shifted to the right side with increasing the solvent acceptor number :

$$\underset{\text{5-coordinate}}{[CuCl(L^2)(tmen)]} \rightleftharpoons \underset{\text{4-coordinate with axial solvation}}{[Cu(L^2)(tmen)]^+} + Cl^-$$

In DCE, the $\tilde{\nu}_{max}$ (x 10^{-3},cm^{-1}) values for [CuCl($\mathbf{L^2}$)(tmen)] and [Cu(acac)Cl(tmen)] are 14.45 and 14.03, respectively.[12] It can be concluded that the ligand field strength of $\mathbf{L^2}$ is stronger than acac. In the case of acac complex, the $\tilde{\nu}_{max}$ value of solid is very similar (14.3 x 10^3) to that in DCE, which means that the complex has same structure in both states : 5-coordinate.[13]

However, in present case, the $\tilde{\nu}_{max}$ in solid is larger than its value in a non-polar solvent such as DCE (Table 1). As it was mentioned before, it can be related to a weak hydrogen-bond interaction which probably exists between O5-H...Cl of two adjacent molecules in crystal and causes a displacement of chloride anion from its position in a regular square pyramid. Then the chelate has the 5-coordinate structure with an axial elongated chloride and the $\tilde{\nu}_{max}$ will be larger than its value in DCE (in which the structure is 5-coordinate, because of absence of this type of intermolecular hydrogen-bonding).

Table 2. Conductivity data for [CuCl(L^2)(tmen)] in different solutions (1.0 x 10^{-3} M , 25 °C)

Solvent	Λ_M ($\Omega^{-1}cm^2mol^{-1}$)	Type of electrolyte
H_2O	108	1:1 electrolyte
MeOH	79.2	
EtOH	30.4	weak electrolyte
DMSO	41.1	
DCE	4.3	non-electrolyte

In non-polar solvents such as DCE, the ε_{max} of complex is higher than its ε_{max} in polar solvents such as MeOH. Usually, higher ε_{max} is characteristic point of 5-coordinate species of the Cu(II) complexes. It also can be related to conductivity of solutions.[14] As we can see in Table 2 , in MeOH, the complex is strongly dissociated; in EtOH and DMSO, the complex shows a partial dissociation (weak electrolyte) which depends on acceptor properties of the solvents used. In DCE (non-polar solvent) almost all of the complex exists in the undissociated form (5-coordinate).

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7 Infrared absorption bands ($\tilde{\nu}$, cm^{-1}) : 3412 s (hydroxyl), 1720 vs, 1693 vs (C=O), 1612 m (enol-keto) .
8 ^{1}H - NMR, δ (ppm) = 7.1(2H,d,J=9Hz), 6.8(2H,d,J=8Hz), 3.97(1H,d,J=2.3Hz),3.7(1H,d,J=12Hz),3.2(1H,d,J=11Hz) 3.77 (3H,s) , 2.6 (1H, d,J =14Hz),2.5(1H,dd,J=14,2.3Hz), 3.92 (1H, t ,J =12Hz) , 1.7 (3H,s) , 2.0 (3H,s) , 1.3 (3H,s) ^{13}C-NMR, δ (ppm) = 215.3,204(d),159,129.9,128.8,114.6, 73.8,68,61.7,55.2,53.5,44.8,34.4,30.2,28.4
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10 Crystallographic data: $C_{25}H_{39}N_2O_5CuCl_3$, formula weight = 617.50, monoclinic, space group Cc(#9), a=11.678(1) Å, b= 22.284(1) Å, c =11.816(1) Å, β=91.00(7), V=3074.3(4) Å^3, Z = 4, D_{calc} =1.334 g.cm^{-3}, R = 0.043, R_w = 0.025 for 2428 reflections with $I = 3\sigma(I)$.
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