



Synthesis and Characterization of the Thiazolidinone and/or Thiourea substituted Amine Complexes of Cu (II)

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<http://dx.doi.org/10.13005/ojc/300464>

(Received: September 09, 2014; Accepted: October 16, 2014)

ABSTRACT

Mixed ligand complexes of copper (II), involving either Mercaptyl thiazolidinone (1) [2-(2-hydroxy benzoyl)-3-N-(2-mercaptyl)-1-Thiazolidin-4-one] or Pyridine thiazolidinone (2) [2-(2-hydroxy benzoyl)-3-N-(2-Pyridinyl)-1-Thiazolidin-4-one] alone and along with Thiourea were synthesized by partial or complete replacement of the strongly coordinated ammonia of ammine complex. All the products have been characterized by elemental analysis, molar conductance, magnetic susceptibility, IR and electronic spectral measurements for their bonding and structures.

Key words: Mixed ligand complexes, Mercaptyl thiazolidinone, Pyridine thiazolidinone, Thiourea, Ammine complexes

INTRODUCTION

Thiazolidinones are the derivatives of thiazolidine which belong to an important group of heterocyclic compounds containing sulphur and nitrogen in a five member ring. The nucleus is also known as wonder nucleus because it gives out different derivatives with all different types of biological activities.

Chemistry of complexes derived by partial or complete replacement of strongly coordinated

ammonia, halogen, cyanide or thiocyanate by organic ligands like Schiff's bases have rare mention ^[1-3] in literature. Products obtained by replacement of ammonia of ammine complexes of copper(II), with 2-(2-hydroxy benzoyl)-3-N-(2-mercaptyl)-1-Thiazolidin-4-one (**1**) or 2-(2-hydroxy benzoyl)-3-N-(2-Pyridinyl)-1-Thiazolidin-4-one(**2**) alone and along with thiourea have not been described hitherto and we now report their synthesis. Product(s), isolated as binary mixture(s) were resolved by column chromatography.

EXPERIMENTAL

Materials and methods

Thiazolidinones (**1**) and (**2**) were prepared by known methods ^[4] of cyclocondensation of respective ketoanils with thioglycolic acid and purified by recrystallization. Ammine complex $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ was prepared and purified by King's methods ^[5]. Metal Chloride and other chemicals (Aldrich, Qualigen and BDH) were used as supplied except solvents which were used after distillation.

Preparation of Complexes

Complexes resulting from partial replacement of coordinated ammonia by (**1**) or (**2**) alone and along with thiourea were prepared by mixing ethanoic solutions of ligands (0.1 mol each) with aqueous ethanoic (70%) solutions of ammine complexes (0.1 mol) in presence of NH_3 (5 cm³). a-fraction of ligand (1) and thiourea substituted ammine complexes of Cu (II) precipitated immediately or after refluxing the reaction mixture (4-6hrs). The products were washed with EtOH/ Me_2CO and dried in hot air oven at 80°C; b-fraction isolated from filtrates on concentration and crystallization was washed with EtOH/AcOH-Toluene(3:1 v/v) Et_2O and dried at 100°C Ligand (II) substituted ammine complexes of Cu(II) crystallized from their reaction mixtures after their 6-12 hrs refluxing from the reaction mixture containing (2), thiourea and $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$, $\text{Cu}_3(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})\text{Cl}_6 \cdot 2\text{H}_2\text{O}$ was precipitated immediately whereas $\text{Cu}(\text{SCN}_2\text{H}_4)(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})\text{Cl}_2 \cdot 5\text{H}_2\text{O}$, was isolated on refluxing, concentrating and crystallizing the filtrate.

Resolution of binary complexes

Chromatography was undertaken in a column (50cm length, 2cm diameter) containing silica gel (50-100 mesh, BDH) in AcOH- C_6H_6 (2:1 v/v). The binary products were dissolved in dimethylsulphoxide and loaded in the column, and the fast moving component eluted. The slow moving component was eluted with an appropriate solvent. Eluates were evaporated to dryness under reduced pressure.

Analysis and Physical Measurements

C, H and N analysis were done on Vario-el-III Element-R. Melting points determined in open

glass capillaries were uncorrected, infrared spectra were recorded on Thermo Nicolet Nexus FT-IR spectrometer in Nujol whereas reflectance spectra were recorded on a Carl-Zeiss VSU-2P spectrophotometer in MgO. Conductometric measurements on standard solutions of complexes in DMSO were made on Toshniwal Conductivity Bridge using a dip-type cell. Magnetic susceptibilities for solids were measured in vibrational magnetometer. Molecular weights were determined by micro Rast's method ^[6] using Camphor solvent.

RESULTS AND DISCUSSION

Analysis and molecular weights data are in conformity of proposed molecular formulae. Silver nitrate test revealed non-electrolytic nature of complexes.

IR spectrum of (1) together with ammonia and thiourea exhibits frequencies of C-N (cyclic), C-S-C (cyclic) and SH groups at 1600 cm⁻¹, 690cm⁻¹ and 2670cm⁻¹ respectively. Considerable lowering in C-N(cyclic) frequency and disappearance of SH band in complexes led to the inference that (1) is coordinated with metal ions through its thiazolidinone ring nitrogen and deprotonated mercaptyl group. New low frequency peaks corresponding to M-N and M-S stretches appeared in the spectra of complexes supported the participation of these groups in coordination. Ligand (2) displays $\nu\text{C}=\text{O}$ (cyclic) and $\nu\text{C}=\text{N}$ (cyclic) vibrations at 1600 cm⁻¹ and 1590cm⁻¹ respectively. In the complexes obtained by partial or complete substitution of ammonia by (2) alone or along with SCN_2H_4 , thiazolidinone ring carbonyl group peak disappeared and pyridine ring C=N group frequency lowered considerably. This suggests coordination of thiazolidinone ring carbonyl oxygen after its enolization and pyridine ring nitrogen. Two new low frequency bands corresponding to M-O and M-N stretches confirm this inference. In the products obtained by partial substitution of ammonia by (1) or (2) an additional band of $\nu\text{M-N}$ is observed. If two nitrogens are coordinated one is from thiazolidinone ring or pyridine ring and other should be from ammonia. The low symmetrical deformation (ca. 1608 cm⁻¹) and rocking(ca. 842 cm⁻¹) vibrations of coordinated ammonia confirm this. In the IR

Table 1: Magnetic Moment and Reflectance Spectra of Complexes

Complexes	Magnetic Moment (μ_{eff})BM	Reflectance Spectra		10Dq(cm ⁻¹)
		Band(cm ⁻¹)	Assignment	
[Cu(NH ₃)(C ₁₆ H ₁₂ NO ₃ S ₂)(H ₂ O) ₂ Cl].4H ₂ O	2.00	12563 15385 23364 24510 25253 26667 27322 40816 47619	² T _{2g} ← ² E _g ² B _{2g} ← ² B _{1g} ² E _g Metal → Ligand Charge Transfer	12563
[Cu(NH ₃)(C ₁₆ H ₁₂ NO ₃ S ₂) ₂ (H ₂ O)].H ₂ O	1.95	12626 12920 27548 28409 34483 35336 40162	² T _{2g} ← ² E _g Metal ← Ligand Charge Transfer	12920
[Cu(NH ₃)(SCN ₂ H ₄)(C ₁₆ H ₁₂ NO ₃ S ₂)(H ₂ O)Cl].H ₂ O	1.89	12579 13106 21786 23202 23810 27933 35336 37879 40323 43668 48780	² T _{2g} ← ² E _g ² A _{1g} ← ² B _{1g} ² B _{2g} ← ² B _g ← Metal ← Ligand Charge Transfer	12579
[Cu ₂ (NH ₃)(C ₁₅ H ₁₁ N ₂ O ₃ S)(H ₂ O) ₃ Cl ₄]	1.67	12920 20964 21552 23529 28248 36232 40816 45455 47170	² T _{2g} ← ² E _g ² A _{1g} ← ² B _{1g} ² B _{2g} ← ² E _g ← Metal ← Ligand Charge Transfer	12920
[Cu ₃ (C ₁₅ H ₁₁ N ₂ O ₃ S)Cl ₆].2(H ₂ O)	1.70	16367 16694 17331 40650 48547	² A _{1g} ← ² B _g ² B _{2g} ← ² E _g ← Metal ← Ligand Charge Transfer	12920
[Cu(SCN ₂ H ₄)(C ₁₅ H ₁₁ N ₂ O ₃ S)(H ₂ O)Cl ₂].4H ₂ O	1.85	12594 12920 26455 27174 28090 40323 47170 50000	² T _{2g} ← ² E _g Metal ← Ligand Charge Transfer	-

spectra of complexes involving (1) or (2), NH_3 and SCN_2H_4 , unperturbed additional ammine frequencies and a new low frequency band (260 cm^{-1}) suggest bonding of SCN_2H_4 through sulphur. Coordination of monodentate chlorine is indicated by $\nu\text{M-Cl}$ band occurring in 300 cm^{-1} - 320 cm^{-1} region whereas chlorine bridged polynuclear structures are supported by either a well-defined $\nu\text{M-Cl-M}$ peak or a broad peak arising by mixing of closely spaced $\nu\text{M-Cl}$ peak. Lattice water exhibits symmetrical and anti-symmetrical stretching and bonding vibrations in 3321 cm^{-1} to 3442 cm^{-1} and 1600 cm^{-1} to 1625 cm^{-1} ranges respectively, whereas coordinated water displays ρ_t , ρ_w and ρ_r vibrations in 825 cm^{-1} - 995 cm^{-1} range. M-OH_2 bands, which generally occur in 200 cm^{-1} to 450 cm^{-1} region, could not be clearly identified owing to presence of $\nu\text{M-N}$, $\nu\text{M-Cl}$ and $\nu\text{M-S}$ bands in this region.

Analytical data of complexes

1. $[\text{Cu}(\text{NH}_3)_2(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})_2\text{Cl}].4\text{H}_2\text{O}$:
Colour : Grey; M.P.: 190°C . Anal Calcd.: C,34.65; H, 4.87; N,5.05. Found: C, 34.72; H,4.87; N,5.05. Mol.wt: Calcd: 554; Found:555. IR(cm^{-1}): $\nu\text{C-N}$ (cyclic), 1500; $\nu\text{C-S-C}$, 702sh; $\nu\text{M-NH}_3$ and/or M-O, 529; $\nu\text{M-N}$, 457; $\nu\text{M-Cl}$, 300; $\nu\text{M-S}$, 270.
2. $[\text{Cu}(\text{NH}_3)_2(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})].\text{H}_2\text{O}$:
Colour : Grey; M.P.: 209°C . Anal Calcd.: C,24.72; H, 2.44; N,5.40. Found: C, 24.77; H,2.85; N,5.40. Mol.wt: Calcd: 777; Found:769. IR(cm^{-1}): $\nu\text{C-N}$ (cyclic), 1505; $\nu\text{C-S-C}$, 650; $\nu\text{M-NH}_3$ and/or M-O, 544; $\nu\text{M-N}$, 457; $\nu\text{M-S}$, 290.
3. $[\text{Cu}(\text{NH}_3)_2(\text{SCN}_2\text{H}_4)(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})\text{Cl}].\text{H}_2\text{O}$:
Colour : Green black; M.P.: 240°C . Anal Calcd.: C,36.55; H, 4.48; N,10.03. Found: C, 35.99; H,4.33; N,10.15. Mol.wt: Calcd: 558; Found:555. IR(cm^{-1}): $\nu\text{C-N}$ (cyclic), 1511; $\nu\text{C-S-C}$, 667; $\nu\text{M-NH}_3$ and/or M-O, 527; $\nu\text{M-N}$,

4. $[\text{Cu}_2(\text{NH}_3)_2(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})(\text{H}_2\text{O})_3\text{Cl}_4]$:
Colour : Brown; M.P : 238°C . Anal Calcd.: C,30.76; H, 2.29; N,7.17. Found: C, 30.92; H,2.20; N,7.22. Mol.wt: Calcd: 585; Found : 588. IR(cm^{-1}) : $\nu\text{C-N}$ (cyclic), 1625br; $\nu\text{C-S-C}$, 675; $\nu\text{C=N}$,1433; $\nu\text{M-NH}_3$ and/or M-O, 500 and 467br; $\nu\text{M-N}$, 417, 467br; $\nu\text{M-Cl}$, 300 and 280.
5. $[\text{Cu}_3(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})\text{Cl}_6].2(\text{H}_2\text{O})$:
Colour : Grey; M.P : $>300^\circ\text{C}$. Anal Calcd.: C,24.37; H, 2.03; N,3.79. Found: C, 24.05; H,2.44; N,3.83. Mol.wt: Calcd: 775; Found : 769. IR(cm^{-1}) : $\nu\text{C-S-C}$, 674; $\nu\text{C=N}$,1449; $\nu\text{M-NH}_3$ and/or M-O, 483br; $\nu\text{M-N}$, 434; $\nu\text{M-Cl}$, 295br.
6. $[\text{Cu}(\text{SCN}_2\text{H}_4)(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})(\text{H}_2\text{O})\text{Cl}_2].4\text{H}_2\text{O}$
Colour : brown; M.P.: 200°C . Anal Calcd.: C,32.02; H, 4.17; N,9.34. Found: C, 31.62; H,4.27; N,9.28. Mol.wt: Calcd: 599; Found:588. IR(cm^{-1}) : $\nu\text{C-N}$ (cyclic), 1608; $\nu\text{C=N}$,1466; $\nu\text{M-NH}_3$ and/or M-O, 500 and 475br; $\nu\text{M-N}$, 417; $\nu\text{M-Cl}$, 305; $\nu\text{M-S}$, 260.

Band frequencies, assignments and values of ligand field parameters obtained by standard treatment⁸ are in table 1.

The magnetic moment and reflectance spectrum of $[\text{Cu}_3(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})].2\text{H}_2\text{O}$ displaying three d-d transition bands in 16367 - 17331 cm^{-1} range, characteristic of D_{4h} symmetry^{1,9}, indicate its square-planar geometry. All other copper (II) complexes displaying one or two broad bands in 12516 - 15385 cm^{-1} range and other two or three bands in 16367 - 24510 cm^{-1} region indicate^[10] their distorted octahedral stereochemistry involving ${}^2T_{2g} \leftarrow {}^2E_g$ transitions; the 2E_g state being susceptible to John-Teller distortion may account for the broad peak structure.

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