



Chemistry of the Thiazolidinone alone or along with Thiourea substituted Amine Complexes of Zinc (II)

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ABSTRACT

Mixed ligand complexes of zinc (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 have been obtained 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 and IR and electronic spectral measurements for their bonding and structures.

Key Words: Mixed ligand complexes, Mercaptyl thiazolidinone,
Pyridine thiazolidinone, Thiourea, Ammine complexes.

INTRODUCTION

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 mention¹⁻³ in literature. Products obtained by replacement of ammonia of ammine complexes of zinc(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

Thiazolidinones (1) and (2) were prepared by known methods ⁴ of cyclocondensation of respective ketoanils with thioglycolic acid and purified by recrystallization. Ammine complex [Zn (NH₃)₄] Cl² 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 cm^3). Ligand (1) substituted ammine complexes of Zn(II) were obtained as binary mixture on refluxing (~6hrs), concentrating and crystallizing the reaction mixture.

Ligand (2) substituted ammine complexes of Zn(II) crystallized from their reaction mixtures after their 6-12 hrs refluxing. Zn (II) involving ligand (1)/ligand (2) and thiourea could not be prepared by the replacement procedure as complete substitution of coordinated ammonia with either one or both ligands proved to be impossible for unknown reasons.

Resolution of binary complexes

Thin-layer chromatography on starch bound silica gel revealed that $\text{Zn}(\text{NH}_3)_2(\text{C}_{16}\text{H}_{11}\text{NO}_3\text{S}_2)\text{Cl}\cdot 2\text{H}_2\text{O}$ was binary mixture. This was quantitatively resolved by column chromatography.

Chromatography was undertaken in a column (50cm length, 2cm diameter) containing silica gel(50-100 mesh, BDH) in $\text{AcOH}\text{-}\text{C}_6\text{H}_6$ (2:1 v/v). Dimethylsulphoxide solution of the binary product was loaded, 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 Variol-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. ^1H NMR spectra were recorded on Perkin Elmer R-32 spectrometer in DMSO using TMS as standard interval. 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 electrolytic nature of complex $\text{Zn}[(\text{NH}_3)_2(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})_2]\text{Cl}$ a- and b- isomers which are 1:1 electrolytes (Λ_m , 52 & 61 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively) .

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} , 690 cm^{-1} and 2670 cm^{-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 1590 cm^{-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.

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 825cm^{-1} - 995cm^{-1} range. M-OH₂ bands, which generally occur in 200cm^{-1} to 450cm^{-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. $[\text{Zn}(\text{NH}_3)_2(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})_2]\text{Cl}$:
Colour: Brown black; M.P.: 200°C . Anal Calcd.: C, 38.36; H, 4.39; N, 8.39. Found: C, 38.17; H, 4.41; N, 8.20. Mol. wt: Calcd: 501; Found: 500. IR(cm^{-1}): $\nu\text{C-N}$ (cyclic), 1570; $\nu\text{C-S-C}$, 669; $\nu\text{M-N}$, 457br; $\nu\text{M-Cl}$, 275; $\nu\text{M-S}$, 275.
2. $[\text{Zn}(\text{NH}_3)_2(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})_2]\text{Cl}$:
Colour: Brown; M.P.: 176°C . Anal Calcd.: C, 38.36; H, 4.39; N, 8.3. Found: C, 39.05; H, 4.11; N, 8.63. Mol. wt: Calcd: 501; Found: 500. IR(cm^{-1}): $\nu\text{C-N}$ (cyclic), 1520; $\nu\text{C-S-C}$, 660; $\nu\text{M-NH}_3$ and/or M-O, 529; $\nu\text{M-N}$, 457; $\nu\text{M-S}$, 290.
3. $[\text{Zn}(\text{NH}_3)_2(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})(\text{H}_2\text{O})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$:
Colour: Black; M.P.: 185°C . Anal Calcd.: C, 35.57; H, 3.95; N, 8.30. Found: C, 35.24; H, 4.13; N, 8.19. Mol. wt: Calcd: 506; Found: 500. IR(cm^{-1}): $\nu\text{C-N}$ (cyclic), 1625br; $\nu\text{C-S-}$

C, 675; $\nu\text{C=N}$, 1449; $\nu\text{M-NH}_3$ and/or M-O, 508sh and 468br; $\nu\text{M-N}$, 417, 468; $\nu\text{M-Cl}$, 315.

4. $[\text{Zn}_2(\text{NH}_3)(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})(\text{H}_2\text{O})_3\text{Cl}_4]$:
Colour: Dark brown; M.P.: 235°C . Anal Calcd.: C, 28.03; H, 3.11; N, 6.54. Found: C, 27.73; H, 2.76; N, 6.59. Mol. wt: Calcd: 643; Found: 645. IR(cm^{-1}): $\nu\text{C-N}$ (cyclic), 1612; $\nu\text{C-S-C}$, 646 and 675; $\nu\text{C=N}$, 1462; $\nu\text{M-NH}_3$ and/or M-O, 515 and 469br; $\nu\text{M-N}$, 457, 469br; $\nu\text{M-Cl}$, 300br

In electrolytic Zn $[(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{NH}_3)(\text{H}_2\text{O})_2]\text{Cl}$ isomers cis- and trans-symmetries may be proposed⁷ for slow-moving-a(R_f , 0.10) and fast-moving-b(R_f , 10.70) components respectively.

Magnetic Moment and Reflectance Spectra of Complexes $[\text{Zn}(\text{NH}_3)_2(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})_2]\text{Cl}$ (a-fraction), $[\text{Zn}(\text{NH}_3)_2(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)(\text{H}_2\text{O})_2]\text{Cl}$ (b-fraction), $[\text{Zn}(\text{NH}_3)_2(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})(\text{H}_2\text{O})\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Zn}_2(\text{NH}_3)(\text{C}_{15}\text{H}_{11}\text{NO}_3\text{S})(\text{H}_2\text{O})_3\text{Cl}_4]$ show that these are diamagnetic in nature .

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