



Synthesis and Characterization of 2-imino-3-(2-Hydroxyphenyl)-1-Thiazolidin-4-one Substituted Ammine Complexes of Cr(III), Co(III), Ni(II) and Cu(II)

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ABSTRACT

Mixed ligand complexes of Cr(III), Co(III), Ni(II) and Cu(II) synthesized by partial substitution of 2-imino-3-(2-hydroxyphenyl)-1-thiazolidin-4-one in respective ammine complexes were characterized by elemental analysis, conductance and magnetic measurements, infrared and uv-visible spectroscopy. Cr(III), Co(III) and Ni(II) complexes were octahedral whereas Cu(II) complex was square planar.

Key words: Mixed-ligand complexes, ligand - substitution reaction, thiazolidinone.

INTRODUCTION

Many metal complexes of biologically important ligands are more effective than their free ligands¹. Mixed ligand complexes have a pivotal role in biological chemistry² as these create specific structures³ and have been implicated in the storage and transport of active substances through membranes. Among these ligands are thiazolidinones, derivatives of thiazolidine. Plenty of thiazolidinone derivatives have been found to exhibit profound broad spectrum of biological properties, viz. bactericidal⁴⁻⁵, fungicidal⁶, anti-convulsant⁷, anti-inflammatory⁸, antitumor⁹, anti-HIV¹⁰ etc. Although reports on synthesis, characterization and biological properties of mixed ligand complexes derived either by direct

interaction¹¹⁻¹⁵ of metal salts with two/three organic donor molecules or by substitution¹⁶ of strong ligand(s) in weakly coordinated ligand of complexes are plenty, ligand exchange reactions^{18,19} involving replacement of strongly coordinated ligands like ammonia, cyanide and thiocyanide by organic ligands such as Schiff's bases alone or alongwith other ligands like thiourea and/or anions are scantily but surprisingly no reference is available on the chemistry of substitution products of thiazolidinone ligands in strongly coordinated ammine complexes hitherto. In view of high biological significance of mixed ligand complexes of biologically important ligands and non-availability of any report on the thiazolidinone substituted ammine complexes as yet, it has been thought worthwhile to synthesize

and characterize mixed ligand complexes by substitution of 2-imino-3-(2-hydroxyphenyl)-1-thiazolidin-4-one in ammine complexes of Cr(III), Co(III), Ni(II) and Cu(II) and report in the present communication.

EXPERIMENTAL

Materials

Chloroacetylchloride, ortho-aminophenol and potassium thiocyanate BDH/Aldrich reagents of 97-99%, purely were used in the synthesis of 2-imino-3-(2-hydroxyphenyl)-1-thiazolidin-4-one (ligand). All the metal chlorides were Analytical grade (BDH) products and used as supplied without further purification.

Physical measurements and analysis

Melting points of the ligand and complexes were determined in open glass capillaries and are uncorrected. The infrared spectra were recorded on Prestige-21 FT-IR spectrophotometer in 4000 cm^{-1} -400 cm^{-1} range in KBr medium. Electronic spectra of complexes were recorded in ethanol on ITEM No - 275 spectrophotometer in 200-800 cm^{-1} range. Magnetic susceptibility measurements were done on MSB-AUTO, (Sherwood Scientific) magnetic balance. The molar conductivity measurements were carried out using Jenway digital conductivity meter. Carbon, hydrogen, nitrogen and sulphur analyses were done on microanalytical Perkin-Elmer 240C elemental analyzer whereas metal analysis was carried out on an atomic absorption spectrometer, Buck Scientific Model 210 VGP AAS. The presence of chloride is established by decomposing the complexes and treating with AgNO_3 .

Synthesis of ligand

The ligand, 2-imino-3-(2-hydroxyphenyl)-1-thiazolidin-4-one, was synthesized by reported method in two steps. In the first step ortho hydroxyphenyl chloroacetanilide, the precursor of the ligand, was synthesized by adding 35 ml chloroacetylchloride dropwise to 0.37 mol of orthoamino phenol in benzene, the precipitate of the product was filtered, washed with benzene and dried in air. In the second step, a mixture containing 2-hydroxyphenyl chloroacetanilide (0.18 mol) and potassium thiocyanate (0.195 mol) in acetone was

refluxed for 5 h. The reaction mixture was filtered after cooling at room temperature and the solvent of filtrate was evaporated on water bath. Finally residue was washed with water repeatedly and dried in air and crystallized from alcohol.

Synthesis of mixed ligand complexes

Ammine complexes of Cr(III)²¹, Co(III)²³, Ni(II)²³ and Cu(II)²⁴ were synthesized by reported methods. With the saturated solution of each of the ammine complex (0.15 mol) in alcohol-water (2:3, v/v) saturated solution of ligand (0.30 mol) in alcohol was mixed and 5 ml concentrated ammonia was added. This reaction mixture was refluxed for 1 h. During refluxing ammonia solution was occasionally added to the reaction mixture to compensate any loss of ammonia. The precipitates obtained, on cooling of the reaction mixtures, were filtered out and washed with ice cold alcohol and dried in air. Purity of the synthesized compounds was checked by TLC.

RESULTS AND DISCUSSION

Analytical and conductivity data of the complexes are presented in table 1. The analytical data correspond to a metal- ligand - ammonia ratio of 1:1:1. The conductivity values in ethanol correspond to 1:1 electrolyte for Cr(III) complex while Co(III), Ni(II) and Cu(II) complexes are non-electrolytes.

The infrared spectra of mixed ligand complexes synthesized are compiled in table 2. The infrared spectra of these complexes in comparison with free ammonia and free ligand show characteristic band positions and shifts which can be correlated to monodentate ammine binding and bidentate chelation respectively. Besides, metal binding through water molecules is also evident from the IR spectra. Free ammonia displays¹⁷. $\nu\text{N-H}$ band in the region 3300-3500 cm^{-1} . In the present complexes IR spectra show characteristics bands in the region 3173-3250 cm^{-1} which are lower compared to those of free uNH_3 . Hence it can be concluded that the nitrogen of ammonia is involved in coordination. The bands occurring at 508 cm^{-1} , 495 cm^{-1} , 522 cm^{-1} and 523 cm^{-1} in Cr(III), Co(III), Ni(II) and Cu(II) complexes respectively, attributed to $\nu\text{M-NH}_3$, strongly support the presence of ammonia in coordination zone of metals.

Table 1: Analytical and conductance data of compounds

| Compounds | Colour | m.p ($\pm 1^\circ\text{C}$) | Elemental Analysis Calculated (Found) % | | | Metal | Molar conductance(Λ_m) ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) |
|--|------------------|----------------------------------|---|-----------------|------------------|-------|--|
| | | | C | H | N | | |
| $\text{C}_9\text{H}_7\text{N}_2\text{O}_2\text{S}$ | Pale yellow | 120 (51.85) | 52.17 (3.54) | 3.38 (13.34) | 13.52 (15.96) | - | - |
| $[\text{CrL}(\text{NH}_3)(\text{H}_2\text{O})_2\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ | Gray | 224 (25.09) | 25.78 (4.11) | 4.29 (10.01) | 10.02 (7.15) | 12.41 | 58.59 |
| $[\text{CoL}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]\cdot \text{H}_2\text{O}$ | Dark brown | 235 (27.21) | 27.72 (4.21) | 3.59 (10.64) | 10.78 (8.16) | 15.00 | 8.57 |
| $[\text{NiL}(\text{NH}_3)(\text{H}_2\text{O})_2\text{Cl}]\cdot 2\text{H}_2\text{O}$ | Brown | 240 (26.98) | 27.69 (4.58) | 4.62 (10.05) | 10.77 (8.02) | 15.05 | 12.35 |
| $[\text{CuL}(\text{NH}_3)\text{Cl}]\cdot 5\text{H}_2\text{O}$ | Green (25.87) | 197 (4.69) | 26.15 (10.16) | 4.84 (8.07) | 10.16 (15.08) | 15.37 | 11.55 |

Where, L = $\text{C}_9\text{H}_7\text{N}_2\text{O}_2\text{S}$

As regards chelation through 2-imino-3-(2-hydroxyphenyl)-1-thiazolidin-4-one ligand, IR spectra exhibit significant features in $\nu\text{O-H}$ (phenolic) and $\nu\text{C-N-C}$ (heterocyclic's) regions. The disappearance of $\nu\text{O-H}$ frequency of free ligand (3410 cm^{-1}) and negative shift in $\nu\text{C-N-C}$ (1329 cm^{-1}) in complexes are clear evidence of coordination of deprotonated phenolic oxygen and heterocyclic ring nitrogen with various metal ions. Weak energy bands occurring in $550\text{-}610\text{ cm}^{-1}$ and $462\text{-}508\text{ cm}^{-1}$ regions of the IR spectra corresponding to $\nu\text{M-O}$ and $\nu\text{M-N}$ respectively substantiate the involvement of deprotonated oxygen of phenolic group and pentacyclic nitrogen of the ligand. Slightly positive changes in $\nu\text{N-H}$ (azomethine) in complex spectra ruled out coordination of azomethine nitrogen.

Lattice water displays symmetrical and asymmetrical stretching and bending vibrations in $3317\text{-}3375\text{ cm}^{-1}$ and $1618\text{-}1664\text{ cm}^{-1}$ regions respectively. The broad peak structure shows overlapping of azomethine $\nu\text{N-H}$ bands. The water of coordination exhibits its characteristic ρ_r , ρ_t , ρ_w vibrations in $837\text{-}916\text{ cm}^{-1}$ range of IR spectra.

The magnetic data pertaining to these systems are depicted in table 3. The magnetic moment of Cr(III) complex is consistent with the spin-free d^3 octahedral geometry involving d^2sp^3 hybridization. The magnetic moment of 2.86 BM of Co(III) complex is very unusual. This value neither corresponds to spin-paired octahedral system nor to a spin - free configuration of the metal in the complex. The observed magnetic moment indicates spin-crossover from high - spin (μ_s 4.89 BM) to low - spin (μ_s 0.00 BM) or vice versa. The Ni(II) complex displaying magnetic moment 2.65 BM, close to high spin d^8 octahedral spin-only value of 2.83 BM with two unpaired electrons. The magnetic moment 1.85 BM of Cu(II) complex is indicative of one unpaired electron in this system.

The electronic spectral data of the complexes are noted in table 3. In the electronic spectra of Cr(III) complex three d-d transition bands observed at 20940 cm^{-1} , 24400 cm^{-1} and 28570 cm^{-1} corresponding ${}^2\text{E}_g \rightarrow {}^4\text{A}_2g$ (F), ${}^4\text{A}_2g \rightarrow {}^4\text{T}_1g$ (F), ${}^4\text{A}_2g \rightarrow {}^4\text{T}_1g$ (P) spin-allowed transitions respectively are consistent with octahedral

Table 2: Infrared spectral data of compounds.

| Compound | $\nu(\text{C}=\text{O})$ | $\nu \text{C-S-C}$ | $\nu(\text{C}=\text{N})$ | $\nu\text{C-N}$ | $\nu\text{N-H}$ of azomet. +NH ₃ | $\nu\text{O-H}$ | $\nu\text{C}=\text{C}$ | Orto Disub stituted | Water coord. M-O | Lattice water $\nu \text{H}_2\text{O}$ | $\nu\text{M-N}$ $\nu \text{H}_2\text{O}$ |
|--|--------------------------|--------------------|--------------------------|-----------------|---|-----------------|------------------------|---------------------------|------------------------|--|---|
| C ₉ H ₈ N ₂ O ₂ S | 1659 | 1596 | 686 715 | 1329 | 3338 | 3410 | 1456 1549 1596 | - | - | - | - |
| [CrL(NH ₃)(H ₂ O) ₂ Cl]Cl·H ₂ O | 1645 | 1600 | 700 | 1283 | 3375 3173 | - | 1456 1600 | 837 | 3375 | 1645 | 610 |
| 508 br [CoL(NH ₃)(H ₂ O)Cl ₂]·H ₂ O | 1618 | 1577 | - | 1276 | 3317 3250 | - | 1466 1577 | 837 | 3317 | 1618 | 590 495 |
| [NiL(NH ₃)(H ₂ O) ₂ Cl]·2H ₂ O | 1664 | 1576 | - | 1277 485 | 3335b 3175 | - | 1466 1576 | 845 916 | 3335 | 1664 | 550 462 522 |
| [CuL(NH ₃)Cl]·5H ₂ O | 1664 | 1576 | - | 1277 | 3341 | - | 1466 1576 | - | 3341 | 1664 | 588 462 523 |

Were, L= C₉H₇N₂O₂S, br = broad, o = ortho

Table 3. Electronic spectra and magnetic data of mixed ligand complexes

| Complex | μ_{eff} (BM) (temp K) | Electronic spectra bands λ_{max} (cm^{-1}) in ethanol |
|--|-------------------------------------|---|
| [CrL(NH ₃)(H ₂ O) ₂ Cl]Cl. 2H ₂ O | 4.22 (294) | 20947(475 nm), 24400(409.8 nm) |
| [CoL(NH ₃)(H ₂ O)Cl ₂]. H ₂ O | 2.86(294) | 28570(350 nm), 41667(240 nm) 15450(647.5 nm), 20964(477 nm) 22716(440 nm),32658(306 nm) |
| [NiL(NH ₃)(H ₂ O) ₂ Cl]. 2H ₂ O | 2.65(294) | 12346(810 nm),14796 (676nm) 15625(640 nm),33113(302 nm) |
| [CuL(NH ₃)Cl].5H ₂ O | 1.87(294) | 15456(645 nm),17319(577 nm) 18501(540.5 nm) 28169(355 nm),46100(217 nm) |

Where, L= C₉H₈N₂O₂S

stereochemistry of this complex. The electronic spectra of Co(III) complex displays multiple bands. First band at 15450 cm^{-1} is assigned ²⁷ to ¹A_{1g} → ³T_{2g}(G) spin-forbidden transition whereas other two bands at 20964 cm^{-1} and 22716 cm^{-1} correspond to ¹A_{1g} → ¹T_{1g}(G) and ¹A_{1g} → ¹T_{2g}(G) spin-allowed transitions respectively of octahedral geometry. Fourth band of high energy attributed to charge transfer from ligand to metal. The electronic spectra of Ni(II) complex show multiple bands, First three of

these bands are assigned³⁰⁻³¹ to spin allowed transitions ³A_{2g} → ³T_{2g}, ³A_{2g} → ³T_{1g}(F) and ³A_{2g} → ³T_{1g}(P) respectively of spin-free d⁸ system. Fourth band of high energy corresponds to charge transfer. First three band of lower energy in the electronic spectra of Cu(II) complex are characteristic ³⁰ of ²B_{1g} → ²A_{1g} (d_{x²-y²} → dz²), ²B_{1g} → ²B_{2g} (d_{x²-y²} → d_{xy}), and ²B_{1g} → ²E_g d-d transitions of square planar geometry, two high energy bands correspond to charge transfer.

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