Chemistry of the thiazolidinone alone or along with thiourea substituted cyanato and thiocyanato complexes

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ABSTRACT

Mixed ligand complexes of Iron(II), Iron(III) and chromium(III) involving either 2-(2-hydroxy benzol)-3-N-(2-mercaptyl)-1-Thiazolidin-4-one[1] or 2-(2-hydroxy benzol)-3-N-(2-pyridinyl)-1-Thiazolidin-4-one[2] alone and along with thiourea have been obtained by partial or complete replacement of the strongly coordinated cyanide and thiocyanate of cyanato and thiocyanato complexes respectively. All the products have been characterized by elemental analysis, molar conductance, magnetic susceptibility and IR and electronic measurement for their bonding and structures.

Key words: Thiazolidinone, Thioura, Thiocyanato complexes.

EXPERIMENTAL

Material and methods
Thiazolidinones (1) and (2) prepared by reported method were purified by recrystallization. Both K\textsubscript{4}Fe(CN)\textsubscript{6} and K\textsubscript{3}Fe(CN)\textsubscript{6} complexes and other chemicals (BDH, Qualigens and CDH) were used as supplied. K\textsubscript{3}Cr(CNS)\textsubscript{6} complex was prepared and purified by King's method.

Preparation of complexes
Ligand (1) substituted thiocyanato complex has prepared by refluxing the reaction containing K\textsubscript{3}[Cr(CNS)\textsubscript{6}] and (1) in acetone-water (8:2, v/v) in 1:2 molar ratio for 10 h; precipitate washed with toluene was dried in hot air at 80°C. A-Fraction of complex involving (1) and Thiourea, obtained as precipitate during refluxing the reaction mixture of K\textsubscript{3}[Cr(CNS)\textsubscript{6}],(1) and Thiourea (1:2:2 molar ratio) in acetone-water (8:2, v/v), was washed with ACOH-MeOH-C\textsubscript{7}H\textsubscript{8} (2:1:2 v/v) and dried at 80°C, whereas its b-fraction was obtained by crystallization of filtrate; washing solvent for b-fraction was the same as for a-fraction. Complex [Cr(CNS)\textsubscript{3}(C\textsubscript{15}H\textsubscript{11}N\textsubscript{2}O\textsubscript{3}S)\textsubscript{2}](H\textsubscript{2}O)\textsubscript{2} was precipitated by adding ether to the

INTRODUCTION

Pursuing our continuous interest in chemistry of mixed ligand complexes derived\textsuperscript{1-3} by substitution of organic ligands in various simple complexes including ammine complexes, a few new complexes which have not been synthesized hitherto are obtained by partial or complete replacement of strongly coordinated cyanide of K\textsubscript{3}Fe(CN)\textsubscript{6} and K\textsubscript{4}Fe(CN)\textsubscript{6} complexes by 2-(2-hydroxy benzol)-3-N-(2-mercaptyl)-1-Thiazolidin-4-one[1] or 2-(2-hydroxy benzol)-3-N-(2-pyridinyl)-1-Thiazolidin-4-one[2] alone and along with thiourea and we now report their synthesis.

Iron complexes in +2 and +3 oxidation could easily from low-spin, high-spin and spin-crossover complexes under the influence of different ligand fields. Spin-crossover complexes generally exhibiting unusual magnetic moments indeed are interesting. Although examples of spin-crossover complexes are scanty\textsuperscript{4-6} With the interest in spin-crossover system we have undertaken Ferro and ferri cyanide complexes for the synthesis of desired products.
refluxed reaction mixture containing (2) and K₂[Cr(CN)₆] 0.2 mol and 0.1 mol respectively in Me₂CO-H₂O (8:2,v/v) and washing the product with AcOH-Et₂O (2:1,v/v) and drying at 80 °C. K₄[Fe₂(CN)₁₀(C₁₅H₁₁N₂O₃S).H₂O resulting from partial replacement of cyanide by (2) was prepared by mixing K₃[Fe(CN)₆] (0.1 mol) and (2) (0.2 mol) in water – EtOH (3:1, v/v) and refluxing the reaction mixture (~8h); precipitate obtained was washed with AcOH-Et₂O (2:1,v/v) and Et₂O successively and dried in over at 65 °C. Ligand(1) substituted product K₆[Fe₂(CN)₉(C₁₆H₁₂NO₃S₂)(H₂O)].5H₂O was obtained as blue solid on mixing (1) and K₄[Fe(CN)₆] in water-AcOH (1:2,v/v) in 1:2 molar ratio, refluxing for 2-3 h, washing the precipitate with AcOH-CHCl₃-MeOH (3:2:2,v/v) and drying at 75 °C. For the preparation of the substitution products of (2) in K₄[Fe(CN)₆], mixture of reactants in water-AcOH (1:2,v/v) in 2:1 molar ratio was refluxed, concentrated and crystallized. Binary solid was dissolved in DMSO. Insoluble K₂[Fe(C₁₅H₁₁N₂O₃S)(CH₃COO)₄].6 H₂O was recovered from filtrate by evaporating the solvent and washing the residue with AcOH-MeOH-C₇H₈ (5:3:2,v/v).

Analysis and physical measurements
C, H and N analysis were done on vario-el-
III Blement-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 on vibrational magnetometer. Molecular weights were determined by micro Rast’s method using camphor solvent.

RESULTS AND DISCUSSION
Analyses and molecular weights data are in fair agreement with suggested molecular formulations of the complexes. All the mononuclear chromium (III) complexes are non-electrolytes, whereas iron complexes are electrolytes; low Λm values generally obtained may be attributed to the presence of large anions.

I.r. spectra displays νC=N(cyclic), νC-S-C and νS-H bands at 1600 cm⁻¹, 690 cm⁻¹ and 2670 cm⁻¹ respectively. Considerable lowering in C-N (cyclic) frequency and disappearance of S-H band in complexes led to the inference that (1) is coordinated with metal ions through its thiazolidinone nitrogen and deprotonated mercaptyl group. Low frequency peaks corresponding of νM-N and νM-S appeared in complex spectra, supported the participation of these groups in coordination. Ligand (2) displays νC=O (cyclic) and νC≡N (cyclic) vibrations at 1600 cm⁻¹ and 1590 cm⁻¹ respectively. In the complexes obtained by partial or complete substitution of thiocyanato or by (2) thiazolidinone carbonyl group peak disappeared and pyridine ring frequency suffered drastic lowering. This suggests coordination of thiazolidinone ring carbonyl oxygen after its enolization and pyridine nitrogen. Two new low frequency bands corresponding to νM-O and νM-N in the complex spectra support this inference.

Thiazolidinone substituted thiocyanato and cyanato complexes, besides ligand bands, displaying well defined peaks of acyclic νC=S, νC-N and δC-N vibrations of thiocyanato and cyanato groups clearly indicate presence of these groups along with (1)/ (2) in coordination zone of metals. Either a single sharp an additional peak of νM-N or a broad peak arising by mixing of two closely spaced peaks of νM-N, one from (1) or (2) and other from thiocyanato or cyanato nitrogen, support the coordination of these groups. K₆[Fe(C₁₅H₁₁N₂O₃S)(CH₃COO)₄].6 H₂O displays asymmetric and symmetric νC-O bands at 1628 cm⁻¹ and 1406 cm⁻¹. The separation of these two bands being greater than that exists in free acetate ion (153 cm⁻¹), indicates monoligancy of acetate ion.

Lattice water displays symmetrical and anti symmetrical stretching and bending vibrations in 3348-3443 cm⁻¹ and 1590-1628 cm⁻¹ ranges respectively, whereas coordinated water exhibits ρ, νo and νt vibrations in 833-980 cm⁻¹ region in the complexes. New low frequency bands corresponding to νM-OH₂ occurring at 459 cm⁻¹ are in conformity of presence of coordinated water in respective complexes.

The splitting patterns in solid state electronic spectra of chromium (III) complexes are
characteristic of high-spin octahedral geometry. The \( \mu_{\text{eff}} \) values are consistent with this. Band frequencies assignments and values of ligand field parameters, 10Dq, Racah's parameters (Band C) and \( \beta \) obtained by standard treatment\(^{11} \) are noted in Table 1. The separation of any two consecutive d-d transitions in [Cr(CNS)(CH\(_4\)N\(_2\)S)(C\(_{16}\)H\(_{12}\)NO\(_3\)S\(_2\))] being greater than in [Cr(CNS)(CH\(_4\)N\(_2\)S)(C\(_{16}\)H\(_{12}\)NO\(_3\)S\(_2\))]\(_2\)H\(_2\)O, cis and trans symmetries respectively may be propose\(^3,10 \) to them.

In order to study spin-crossover phenomenon in Fe(II) and Fe(III) complexes their room temperature magnetic moments were critically examined. The \( \mu_{\text{eff}} \) values of K\(_6\)[Fe\(_2\)(CN)\(_{10}\)(C\(_{15}\)H\(_{11}\)N\(_2\)O\(_3\)S)]\(_2\)H\(_2\)O (1.94 BM) and K\(_6\)[Fe(C\(_{15}\)H\(_{11}\)N\(_2\)O\(_3\)S)(CH\(_3\)COO)]\(_5\)H\(_2\)O (1.92 BM), lying between spin-only values for spin-paired and spin-free octahedral geometries, are suggestive of low-spin to high-spin crossover phenomenon in them whereas \( \mu_{\text{eff}} \) values (4.22 BM) of K\(_6\)[Fe\(_2\)(CN)\(_{10}\)(C\(_{16}\)H\(_{12}\)NO\(_3\)S)(H\(_2\)O)]\(_5\)H\(_2\)O indicates high-spin to low-spin crossover in this Fe(II) complex. Magnetic moment 2.58 BM of K\(_6\)[Fe\(_2\)(CN)\(_9\)(C\(_{16}\)H\(_{12}\)NO\(_3\)S)(H\(_2\)O)]\(_5\)H\(_2\)O, lying between spin-only values for \( S=1/2 \) and \( S=5/2 \) states, indicates low-spin to high-spin crossover in this Fe(II) octahedral complex. The bands splitting pattern in the reflectance spectra, characteristic of \( d^5 \) spin-paired octahedral stereochemistry, indicating predominance of this form, is consistent with suggested spin-crossover in this complex.

REFERENCES