

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

ARCHANA SEXENA*, RAJ KUMAR UPADHYAY and SANIDHYA UPADHYAY

Department of Chemistry, N.R.E.C. College, Khurja - 203 131 (India).

(Received: August 03, 2010; Accepted: September 21, 2010)

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 or 2-(2-hydroxy benzol)-3-N-(2-pyridinyl)-1-Thiazolidin-4-one alone and alongwith 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, Thiourea, Thiocyanato complexes.

INTRODUCTION

Pursuing our continuous interest in chemistry of mixed ligand complexes derived¹⁻³ 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 $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ and thiocyanate of $K_3Cr(CNS)_6$ 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 form 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 scanty⁴⁻⁶. With the interest in spin-crossover system we have undertaken Ferro and ferri cyanide complexes for the synthesis of desired products.

EXPERIMENTAL

Material and methods

Thiazolidinones (1) and (2) prepared by reported method⁷ were purified by recrystallization. Both $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ complexes and other chemicals (BDH, Qualigens and CDH) were used as supplied. $K_3Cr(CNS)_6$ complex was prepared and purified by King's method⁸.

Preparation of complexes

Ligand (1) substituted thiocyanato complex has prepared by refluxing the reaction containing $K_3[Cr(CNS)_6]$ 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 $K_3[Cr(CNS)_6]$, (1) and Thiourea (1:2:2 molar ratio) in acetone-water (8:2, v/v), was washed with ACOH-MeOH- C_7H_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 $[Cr(CNS)_3(C_{15}H_{11}N_2O_3S)(H_2O)]$ was precipitated by adding ether to the

refluxed reaction mixture containing (2) and $K_3[Cr(CNS)_6]$ 0.2 mol and 0.1 mol respectively in Me_2Co-H_2O (8:2,v/v) and washing the product with $AcOH-Et_2O$ (2:1,v/v) and drying at 80 °C. $K_4[Fe_2(CN)_{10}(C_{15}H_{11}N_2O_3S).H_2O]$ resulting from partial replacement of cyanide by (2) was prepared by mixing $K_3[Fe(CN)_6]$ (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 $AcOH-Et_2OH$ (3:1, v/v) and Et_2O successively and dried in over at 65 °C. Ligand(1) substituted product $K_6[Fe_2(CN)_9(C_{16}H_{12}NO_3S_2)(H_2O)].5H_2O$ was obtained as blue solid on mixing (1) and $K_4[Fe(CN)_6]$ in water- $AcOH$ (1:2,v/v) in 1:2 molar ratio, refluxing for 2-3 h, washing the precipitate with $AcOH-CHCl_3-MeOH$ (3:2:2,v/v) and drying at 75 °C. For the preparation of the substitution products of (2) in $K_4[Fe(CN)_6]$, 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 $K_6[Fe_2(CN)_{10}(C_{15}H_{11}N_2O_3S)].H_2O$ washed with water was dried in air; $K_2[Fe(C_{15}H_{11}N_2O_3S)(CH_3COOH)_4].6H_2O$ was recovered from filtrate by evaporating the solvent and washing the residue with $AcOH-MeOH-C_7H_8$ (5:3:2,v/v).

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 on vibrational magnetometer. Molecular weights were determined by micro Rast's method⁹ 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 Δ_m values generally obtained may be attributed to the presence of large anions.

I.r. spectra displays $\nu C-N$ (cyclic), $\nu C-S-C$ and $\nu S-H$ 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 $\nu M-N$ and $\nu M-S$ appeared in complex spectra, supported the participation of these groups in coordination. Ligand (2) displays $\nu C=O$ (cyclic) and $\nu C=N$ (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 $\nu M-O$ and $\nu M-N$ in the complex spectra support this inference.

Thiazolidinone substituted thiocyanato and cyanato complexes, besides ligand bands, displaying well defined peaks of acyclic $\nu C-S$, $\nu C-N$ and $\delta C-N$ 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 $\nu M-N$ or a broad peak arising by mixing of two closely spaced peaks of $\nu M-N$, one from (1) or (2) and other from thiocyanato or cyanato nitrogen, support the coordination of these groups. $K_2[Fe(C_{15}H_{11}N_2O_3S)(CH_3COO)_4].6H_2O$ displays asymmetric and symmetric $\nu C-O$ 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 $3348-3443\text{ cm}^{-1}$ and $1590-1628\text{ cm}^{-1}$ ranges respectively, whereas coordinated water exhibits ν_p , ν_w and ν_r vibrations in $833-980\text{ cm}^{-1}$ region in the complexes. New low frequency bands corresponding to $\nu M-OH_2$ occurring at $Ca.459\text{ cm}^{-1}$ 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 μ_{eff} values are consistent with this. Band frequencies assignments and values of ligand field parameters, $10Dq$, Racah's parameters (Band C) and β obtained by standard treatment¹¹ are noted in Table 1. The separation of any two consecutive d-d transitions in $[\text{Cr}(\text{CNS})(\text{CH}_4\text{N}_2\text{S})(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)]$, being greater than in $[\text{Cr}(\text{CNS})(\text{CH}_4\text{N}_2\text{S})(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S}_2)].2\text{H}_2\text{O}$, cis and trans symmetries respectively may be proposed^{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 μ_{eff} values of $\text{K}_6[\text{Fe}_2(\text{CN})_{10}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})].\text{H}_2\text{O}$ (1.94 BM) and

$\text{K}_2[\text{Fe}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})(\text{CH}_3\text{COO})_4].6\text{H}_2\text{O}$ (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 μ_{eff} values (4.22 BM) of $\text{K}_6[\text{Fe}_2(\text{CN})_9(\text{C}_{16}\text{H}_{12}\text{NO}_3\text{S})(\text{H}_2\text{O})].5\text{H}_2\text{O}$ indicates high-spin to low-spin crossover in this Fe(II) complex. Magnetic moment 2.58 BM of $\text{K}_4[\text{Fe}_2(\text{CN})_{10}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_3\text{S})].\text{H}_2\text{O}$, lying between spin - only values for $S=1/2$ and $S=5/2$ states, indicates low-spin to high-spin crossover in this Fe(III) 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

1. R.K. upadhyay, *J.Indian Chem. soc.* **74**: 214 (1997).
2. R.K. upadhyay, *J.Indian Chem.soc.***75**: 535 (1997).
3. R.K. upadhyay, A.K. Bajpai and K.Rathore, *Transition Met Chem.* **10**: 24 (1985).
4. B.K. Kanungo, B.Pradhan and D.V. Ramana Rao, *J.Indian Chem. Soc.* **63**: 2439 (1986).
5. M.Elizabathe and P.S.Zacharias, *Indian J.Chem.* **24A**, 936 (1985).
6. R.K.upadhyay and A.Rani, *Acta Chi mica Hungarica* **126**: 195 (1989).
7. R.K.upadhyay, N.Agarwal and N.Gupta, *J.Indian Chem. Soc.* **70**: 537 (1993).
8. A. King in A.J.E. Welch (Ed.), 'Inorganic preparation', Allen and Union, London (1950).
9. S.Glasston, 'A text Book of Physical chemistry', Macmillan & co. London (1950).
10. J.Levis and R.G.Wilkins, 'Modern Coordination Chemistry', Interscience, N.Y (1964).
11. E.Konig, 'Structure and Bonding', 175(1971).