Mossbauer Spectral Studies of Some Fe(III)-Ketoanil Complexes

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Studies incorporated in this communication are related to the chemical aspects of high and low spin Fe(III) complexes involving some previously synthesized complexes of hexadentate heterocyclic ketoanil *p*-phenyldianil of 2-thiophenglyoxal (PDATG) along with different anionic ligands, which include the ascertainment of stereochemistries and nature of metal-ligand bonds in the complexes as indicated in our previous findings.

INTRODUCTION

Iron chemistry is, indeed, very interesting primarily because iron has an incomplete 3*d* shell and enters into chemical combination in various valency states such as Fe^0, Fe^{2+}, Fe^{3+}, Fe^{4+}, Fe^{6+}. It also forms a wide variety of low spin complexes in which it exists as Fe(II) and Fe(III). In view of this wide variety of valence states and electronic configurations with which iron can exist in different chemical compounds, the isomer shift data for ^{57}Fe display in a striking manner the power of the Mossbauer tool in the analysis of the chemical bond.

Survey of Mossbauer spectral reports reveals that a large number of investigation have been conducted in iron containing materials[1-6] and coordination complexes[7-14] involving variety of ligands. Critical study of references dealing with applications of Mossbauer spectroscopy in chemistry shows that coordination complexes involving Schiff's base ligands have been examined more than those involving other type of ligands. It is, however, interesting to note that Mossbauer spectra of high spin octahedral Fe(III) complexes of a few bidentate ketoanils have been interpreted[15] for their symmetry and some other chemical properties. The little knowledge in ketoanil complexes of Fe(II) and Fe(III) Mossbauer active nuclei provide a wide field of chemical investigations in this class of compounds by Mossbauer tool.

In continuation of our earlier work[16] of synthesizing and characterizing of seven Fe(III) complexes with ketoanil Schiff base *p*-phenyldianil of 2-thiophenglyoxal (PDATG) by analytical analyses, IR, ESR. Magnetic behaviour[17] of these complexes was further studied on the inferences of magnetic studies ligand field symmetry

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around the central metal ions *i.e.*, stereochemistry of complexes and type of hybridization of metal-ligand orbitals. We now report the Mossbauer studies of all the seven complexes involving PDATG, which include stereochemistry and nature of metal-ligand bonds in the complexes as indicated by other methods.

EXPERIMENTAL

Mossbauer spectra of all the seven Fe(III) complexes were recorded with multi-channel Mossbauer-spectrometer having constant acceleration by using pulverized samples. The source used for taking the spectra was ^{57}Co isotope in palladium matrix which was maintained at room temperature. The velocity calibration was done by using a typical four finger Mossbauer spectrum of a standard enriched with iron absorber. For all spectral analyses source was mounted on the drive while different samples were kept fixed in front of it. Every time sufficient counts were stored in each channel to minimize statistical errors. The Mossbauer spectrum of each Fe(III) complex was recorded at room temperature in Physics Department, University of Roorkee, Roorkee. The values of Mossbauer parameters were determined by inspection with an accuracy of ± 0.01 mm/s.

There are essentially two parameters namely, isomer shift (also called as chemical isomer shift or centre shift) and quadrupole splitting. In the Mossbauer spectrum the difference between the velocities of two peaks gives the measure of quadrupole splitting whereas the distance of the centroid of the quadrupole distance from zero velocity gives the isomer shift.

Magnitude of isomer shift depends in the difference between the radii of the nucleus in the excited and the ground states, $(R_{ex} - R_g)$. The relation is of the following form:

$$\text{Isomer shift} = k(\rho_{ex}^2 - \rho_g^2)\left(\frac{R_{ex} - R_g}{R_g}\right)$$

where, ρ_{ex} and ρ_g are the *s*-electron densities at the nucleus in the excited and ground states and R_{ex} and R_g are isomer radii of the nucleus in the excited and the ground states, respectively. K is a constant. The sign of isomer shift depends on whether R_{ex} is larger or smaller than R_g and on increase in the density produces a negative shift. Consequently $(R_{ex} - R_g/R_g)$ is constant and the isomer shift can thus be used to determine relative densities of s-electron.

The quadrupole splitting (E_Q) arises from the interaction of ^{57}Fe nuclear quadrupole moment (Q) with an electric field gradient (e_g). For example, in the region of the nucleus it is given by the relation:

$$\Delta E_Q = \frac{1}{2}e_g^2 Q\left(1 + \frac{1}{3}\eta^2\right)^{1/2}$$

where, η = symmetry parameter[18].

RESULTS AND DISCUSSION

The electronic configuration of iron atom is $3d^6\,4s^2$ and in the high spin ferrous and ferric states, the configuration would be $3d^6$ and $3d^5$, respectively. It can be readily observed that s-electron configuration in both types of ions would be the same i.e., ($1s^2$, $2s^2$, $3s^2$) and normally if no screening effects due to $3d$ or $3p$ electrons or mutual screening effects were to occur then isomer shift for the ferrous ion would be identical with the isomeric shift of the ferric ion. However, various studies have brought out that isomer shift of the high spin ferrous and ferric compounds are widely differing on account of either difference in oxidation numbers or coordination numbers for symmetries of ligand field. Isomer shift values for high spin Fe^{2+} ions are always higher than high spin Fe^{3+} ions under identical environmental and stereochemical conditions. Under identical ligand(s) environment in both high spin ferrous and ferric ions coordination has significant effect on isomer shift; octahedral high spin Fe(III) compounds exhibit isomer shifts in the range 0.4 mm/s-0.9 mm/s which are higher than the values obtained (0.28-0.32 mm/s) for tetrahedral compounds involving high spin d^5 configuration. Ligand(s) electronegativity or polarizability i.e., ionicity of the coordinate (metal-ligand) bond has been found to be inversely correlated with isomer shift.

From the Mossbauer spectra of Fe(III) complexes, the value of Mossbauer parameters, isomer shift and quadrupole splitting have been calculated as recorded in Table-1.

TABLE-1
ISOMER SHIFT AND QUADRUPOLE SPLITTING DATA OF
Fe(III) COMPLEXES AT ROOM TEMPERATURE

Complex	Isomer shift (nm/s)	Quadrupole splitting (nm/s)
Fe(III)-Cl-PDATG	0.3373	0.6035
Fe(III)-Br-PDATG	0.3905	0.6390
Fe(III)-I-PDATG	0.0178	0.6745
Fe(III)-SO_4-PDATG	0.4260	0.5680
Fe(III)-CNS-PDATG	0.0533	0.3905
Fe(III)-NO_3-PDATG	0.3728	0.5325
Fe(III)-CH_3COO-PDATG	0.4083	0.7455

(Values are with respect to natural iron foil).

Most of the experimental isomer shift values of Fe(III) complexes seem to be unusual. Results of Fe(III)-SO_4-PDTAG and Fe(III)-CH_3COO-PDATG are corresponding to octahedral high spin, d^5 configuration of Fe(III) ion in these complexes. Isomer shift value of Fe(III)-Br-PDATG, though, is slightly lower than that expected for high spin octahedral d^5 configuration could only be attributed to high spin octahedral geometry of this Fe(III) complex and lowering may be accounted for considering tetragonal distortion in the proposed stereochemistry. Values of isomer shifts for Fe(III)-Cl-PDATG and Fe(III)-NO_3-PDATG which are considerably lower than those

expected for high spin octahedral. Fe(III) complexes reveal that both the solids are equilibrium mixtures of low spin and high spin octahedral d^5 configurations. Presence of low spin configuration along with the high spin state may logically be accounted for considering strong ligand fields of NO_3^- and Cl^- ions. Very low isomer shift values of Fe(III)-I-PDATG and Fe(III)-CNS-PDATG complexes are lying in the range of values exhibited by octahedral Fe(III) complexes involving low spin d^6 configuration. Most probably I^- and CNS^- ligands have reduced ferric ion to ferrous state in the complexes and strong field of these ligands has brought *d*-electrons in maximum pairing. More or less the same inferences have come from the values of the quadrupole splitting.

An examination of Mossbauer spectra shows triplet structure of broad quadrupole interaction patterns revealing non-symmetrical arrangements of coordinating groups around Mossbauer nucleus leading to different origins of quadrupolar interactions.

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