Mössbauer study of some biological iron complexes

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Abstract. Some biological complexes containing iron are investigated experimentally at room temperature using the Mössbauer resonance. The complexes show quadrupole doublet and Kramer's degeneracy is found to exist. The electric field gradient, difference in s-electron densities and quadrupole coupling constant have been calculated in each case. These parameters are used to obtain information on the surroundings of the Mössbauer atom.

Keywords. Biological complexes; Mössbauer parameters; hyperfine field parameters.

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1. Introduction

The biological complexes are well-studied using various techniques and it is an established fact that their properties are due to varied geometrical arrangement of ligands around the metal ion [1–4]. Many biological molecules contain iron. The Mössbauer effect provides a powerful probe to chemical state and the environment of iron atoms [5].

The complexes chosen for these investigations are newly synthesized species with different ligands attached to iron metal which is a Mössbauer probe. The ligands used are Schiff bases and they are important because of their wide applicability. These complexes are used as drug derivatives, occurring industrially, biologically, etc. They are also used as metal binding sites in substantial array of metalloproteins in biological systems [6–8]. Thus, these biological complexes are thought to be interesting for the Mössbauer investigations [5] as the determination of hyperfine field parameters will reflect several important physical aspects at the microscopic level.

From the investigations of the complexes, the difference in s-electron densities, quadrupole coupling constant (QCC) and electric field gradient are calculated, assuming the asymmetry parameter (η) to be zero. The knowledge of QCC gives information about coordination number of the complexes [9]. It is a fact that as the coordination number increases, the s-electron charge distribution around the

metal ion tends to be spherically symmetric and, therefore, quadrupole coupling constant decreases.

2. Experimental details

All the samples were examined in the powder form. The Mössbauer data were taken with ^{57}Co diffused into a Rh matrix supplied by the Inter University Consortium for the Department of Atomic Energy Facilities (DAEF), Indore (M.P.), India. The experiment was performed at room temperature (about 300 K). The absorber was kept stationary and the source was moving with velocity ranging from 0 to ± 10 mm/s. All the spectra were taken without an applied magnetic field and they are found to have quadrupole doublet. The isomer shift is found positive in each case. The experimental results (linewidth, area of the line, quadrupole splitting and isomer shift) are shown in table 1. The complexes were examined for crystalline/amorphous nature through XRD. It is found that except $C_8H_{14}N_6FeCl_3O_6$, all other complexes are amorphous.

3. Experimental results and discussion

The Mössbauer spectra of all the complexes were taken at room temperature (about 300 K) as shown in figures 1–5. The Mössbauer parameters are summarised in the table [9,10]. The isomer shift is found to be maximum in complex No. 1 $(1.737536 \times 10^{-8}$ eV) and minimum in complex No. 3 $(1.017152 \times 10^{-8}$ eV). The magnitude of isomer shift is comparable to the reported data at room temperature for various Fe(III) and Fe(II) complexes having hexa coordination around the metal ion [11,12].

The spectra of quadrupole splitting at room temperature suggest that the presence of electric field gradient at the metal ion is due to the presence of ligand around
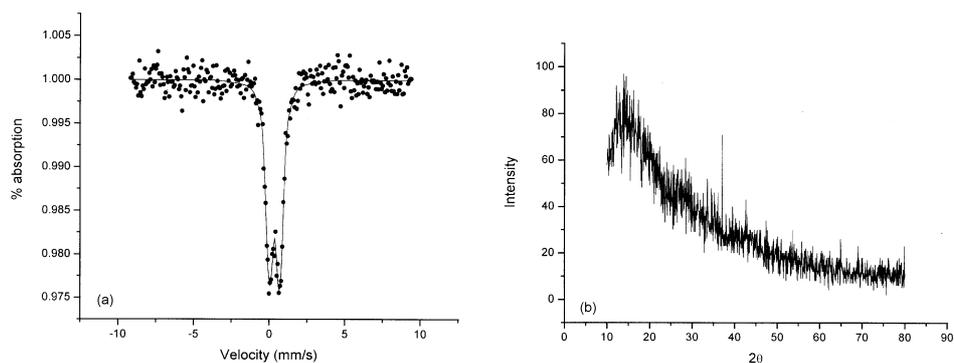

Figure 1. (**a**) The Mössbauer spectrum of the complex $C_{48}H_{50}N_{10}Fe_2Cl_6O_8$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (**b**) X-ray diffraction pattern of the complex $C_{48}H_{50}N_{10}Fe_2Cl_6O_8$.
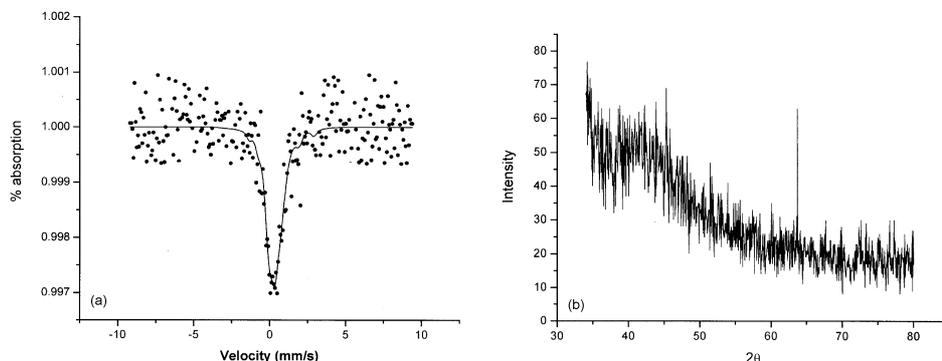
Figure 2. (**a**) The Mössbauer spectrum of the complex $C_{42}H_{56}N_{12}Fe_2Cl_4O_8$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (**b**) X-ray diffraction pattern of the complex $C_{42}H_{56}N_{12}Fe_2Cl_4O_8$.
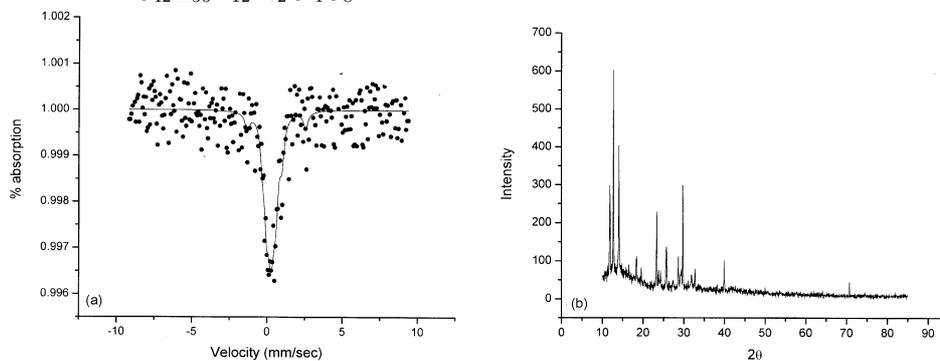

Figure 3. (**a**) The Mössbauer spectrum of the complex $C_{18}H_{14}N_6FeCl_3O_6$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (**b**) X-ray diffraction pattern of the complex $C_{18}H_{14}N_6FeCl_3O_6$.

the ion. This may also be due to some distortion from the perfect octahedral geometry to an elongated octahedral geometry attained by the complex. It is interesting to note that the quadrupole splitting in complexes 1, 4 and 5 are much higher than that in complexes 2 and 3 (table 1). This seems plausible in view of the molecular mode examination of the ligands of complexes 1, 4 and 5, which may provide asymmetric hexa coordination to metal ions *vis-à-vis* that possible for the ligands of complexes 1, 4 and 5. It means that the electric field gradient is significant. Since magnetic splitting does not appear in these complexes, it is suggested that the internal magnetic field is absent at the Mössbauer nuclei in each case and the states remain doubly degenerate, showing the Kramer's degeneracy.

It is seen that the linewidths of the complexes are found large in comparison to the natural linewidth (4.665×10^{-9} eV) of ^{57}Fe. The linewidth is found to be maximum for complex 2 (39.43454×10^{-9} eV) and minimum for complex 1 (26.51958×10^{-9} eV) (table 1). The observation of deviation from the natural linewidth might be trivial and could be due to Doppler broadening of an improper
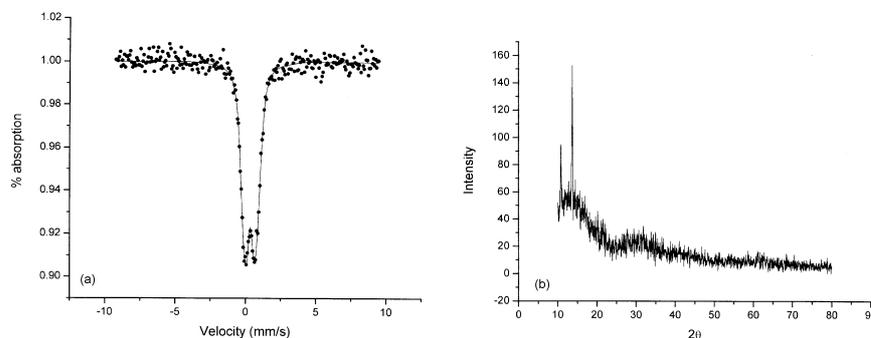
Figure 4. (a) The Mössbauer spectrum of the complex $C_{11}H_{24}N_5S_2FeCl_2$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (b) X-ray diffraction pattern of the complex $C_{11}H_{24}N_5S_2FeCl_2$.
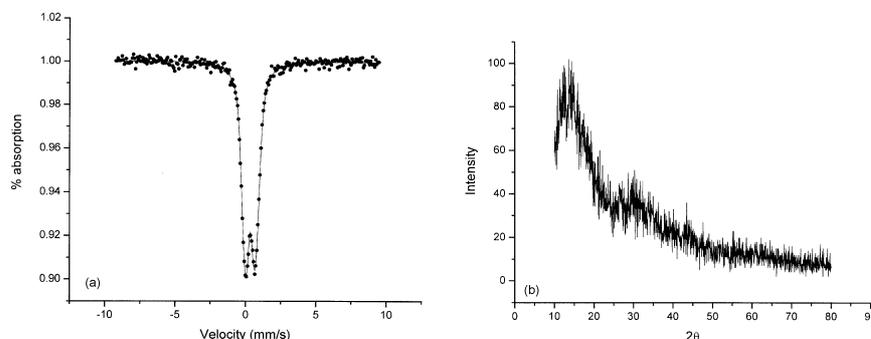

Figure 5. (a) The Mössbauer spectrum of the complex $C_{11}H_{24}N_3S_2Fe(NO_3)_3$ at room temperature. The solid circles are experimental data points and the solid line is fitted to them. (b) X-ray diffraction pattern of the complex $C_{11}H_{24}N_3S_2Fe(NO_3)_3$.

functioning of Mössbauer apparatus (vibration) or saturation effects in the absorber or in the source. However, there are also a number of inherent physical processes causing line broadening.

4. Conclusion

The investigations of these complexes have been carried out to understand the position of the metal (Mössbauer nucleus) within the complexes under investigation. This information can be obtained from the following arguments.

If the electric field gradient (EFG) is highly symmetric at the Mössbauer site then the quadrupole splitting (QS) is insignificant. QS is absent in complexes 2 and 3. It is suggested that the metal ion is surrounded by the same type of ligands having cubic symmetry. This situation arises in closed chain complexes as shown in the Mössbauer spectra in figures 2 and 3. In complex 1, the Mössbauer spectrum (figure 1) reveals that the surrounding ligands are distorted and, therefore, appears

Table 1. The linewidth, isomer shift, quadrupole splitting, electric field gradient, quadrupole coupling constant and Δs-electron density are obtained through the computer analysis at room temperature of the iron complexes ($1\ \mathrm{eV} = 2.080014 \times 10^7$ mm/s).

Properties	1 $C_{48}H_{50}N_{10}Fe_2Cl_6O_8$	2 $C_{42}H_{56}N_{12}Fe_2Cl_4O_8$	3 $C_{18}H_{14}N_6FeCl_3O_6$	4 $C_{11}H_{24}N_5S_2FeCl_2$	5 $C_{11}H_{24}N_3S_2Fe(NO_3)_3$
Linewidth $\times 10^{-8}$ (eV)	2.651958 ± 0.071735	3.943454 ± 0.552174	3.124878 ± 0.395815	3.339521 ± 0.067918	3.0803880 ± 0.0245575
Area of the line $\times 10^{-8}$ (eV)	0.182648 ± 0.003341	0.023692 ± 0.001529	0.023567 ± 0.001721	0.855513 ± 0.009183	0.826816 ± 0.004490
Isomer shift $\times 10^{-8}$ (eV)	1.737536 ± 0.046995	1.415394 ± 0.182422	1.017152 ± 0.139321	1.641460 ± 0.023798	1.634479 ± 0.016620
Quadrupole splitting $\times 10^{-8}$ (eV)	3.209084 ± 0.064557	2.325186 ± 0.341079	2.096837 ± 0.254460	3.488962 ± 0.042961	3.339828 ± 0.017999
Electric field gradient $\times 10^{21}$ V/m^2	3.209084 ± 0.064557	2.325186 ± 0.341079	2.096836 ± 0.254451	3.488962 ± 0.042961	3.339785 ± 0.017999
Quadrupole coupling constant $\times 10^{-8}$ (eV)	0.534847 ± 0.010759	0.387531 ± 0.0568465	0.349473 ± 0.042408	0.581494 ± 0.007160	0.556631 ± 0.003000
Δs-electron density $\times 10^{21}$ c/m^3	10.858623 ± 0.293692	8.845414 ± 1.140031	6.356621 ± 0.870601	10.25820 ± 0.148720	10.21457 ± 0.103860
Grain size	Amorphous	Amorphous	10.162859 Å	Amorphous	Amorphous
Colour of the compound	Dark-brown	Blackish brown	Brown	Reddish-dark brown	Dark-brown

QS. A contribution towards EFG in this case comes from the ligands beyond the closest group of ligands.

In the open chain complexes ligands have no spherical symmetry and as a result, the EFG set up by such a group of ligands is asymmetric, leading to QS as shown in the Mössbauer spectra in figures 4 and 5 of the open chain complexes 4 and 5, respectively. This investigation has a very important application which is given below.

Removal of metal toxicity

When the metal is perfectly encapsulated in the cavity of the macrocyclic ligands it will give a symmetrical environment leading to non-splitting (figures 2a and 3a). Therefore, such a system can be exploited to be used as a pharmaceutical agent to remove the metal toxicity if created in the human or living being systems by complexation phenomenon. This reagent can be administered to remove the excess metal toxicity from the body as metal toxicity is hazardous to living beings.

Acknowledgments

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