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The Mössbauer Effect of Several Iron(II) Octahedral Complexes of α-Dioxime

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The Mössbauer effect has been used to study the electronic structure of iron porphyrins. The measurement is, however, difficult because of the small quantities of iron present. Therefore, an empirical approach, using simple model compounds, appears to be necessary. Since bis(dimethylglyoximato)diimidazoleiron(II) possesses unsaturated equatorial ligands containing nitrogen donor atoms and biologically-important axial ligands, it is regarded as a model complex of iron porphyrins.

We have studied the electronic structure of iron(II)-α-dioxime complexes containing pyridine or imidazole as axial ligands by Mössbauer spectroscopy and will report the results here.

Experimental

1,2-Cyclohexadione-dioxime(CdH_2), dimethylglyoxime(DgH_2), α-furyldioxime(FrH_2), and α-benzyldioxime(BzH_2) were used as the equatorial ligands, and pyridine(Py) and imidazole(Im), as the axial ligands. The pyridine complexes were synthesized as has been described by Matsumoto *et al.*,[1] while the imidazole adducts were prepared by analogous procedures.

The Mössbauer spectra were obtained with scanning velocity spectrometers operating in the time mode. The radiation source was ^{57}Co diffused into a copper or palladium foil and kept at room temperature throughout the measurements. The powdered samples, containing about 8 mg/cm^2 of natural iron, were mounted on aluminum foil, and the spectra were taken at 77 K, at *ca.* 100 K, and at room temperature. The velocity scale was calibrated with metallic iron, and the velocity was determined to an accuracy of ±0.04 mm/s.

Results and Discussion

The isomer shift, δ, and the quadrupole splitting, ΔE_Q, are listed in Table 1. Some typical Mössbauer spectra of bis(α-furyldioximato)dipyridineiron(II) are shown in Fig. 1.

Isomer Shift. The isomer shift of the present samples lies within a range normally found for low-spin complexes.[2] The complexes with α-furyldioxime

TABLE 1. MÖSSBAUER PARAMETERS OF $Fe(II)(\alpha\text{-dioxime})_2X_2$

Compound	Temp. (K)	Quadrupole splitting mm/s	Isomer shift mm/s
$Fe(II)(DgH)_2Py_2$	300	1.78	0.24
	~100	1.73	0.26
$Fe(II)(CdH)_2Py_2$	300	1.76	0.28
	~100	1.80	0.36
$Fe(II)(FrH)_2Py_2$	300	1.90	0.19
	~100	1.87	0.24
$Fe(II)(BzH)_2Py_2$	300	1.91	0.19
	~100	1.94	0.22
$Fe(II)(DgH)_2Im_2$	300	1.31	0.27
	~100	1.29	0.31
$Fe(II)(CdH)_2Im_2$	300	1.38	0.23
	~100	1.36	0.30
$Fe(II)(FrH)_2Im_2$	300	1.44	0.21
	77	1.41	0.25
$Fe(II)(BzH)_2Im_2$	300	1.53	0.21
	77	1.56	0.26

Values of the isomer shift are quoted relative to iron,

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1) C. Matsumoto, Y. Yamane, and K. Shinra, *Nippon Kagaku Zasshi*, **89**, 44 (1968).

2) J. F. Duncan and R. M. Golding, *Quart. Rev.*, **19**, 36 (1965).

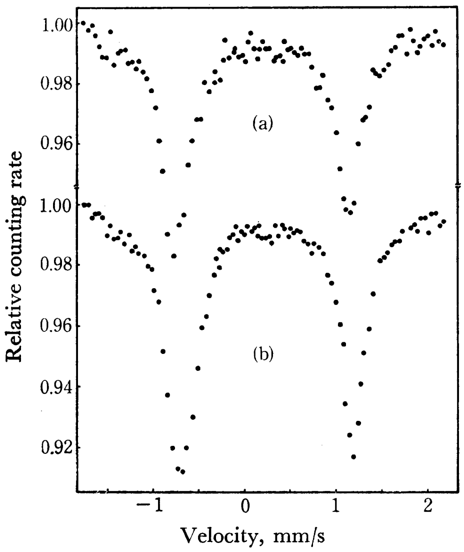

Fig. 1. Mössbauer spectra of $\mathrm{Fe(II)(FrH)_2Py_2}$.
(a) room temperature (b) about 100 K

or α-benzyldioxime exhibit a smaller isomer shift than those with dimethylglyoxime or 1,2-cyclohexadionedioxime. Changes in the isomer shift reflect (a) changes in the s orbital populations due to involvement in covalent bonding, and (b) changes in the shielding of electrons in s orbitals by other electrons, notably those in 3d orbitals whose population and distribution are affected by the details of bonding. α-Furyl and α-benzyl groups, which are π-electron-attractive groups, will lead to a stronger interaction between the 3d orbitals of the central iron and the π* orbitals of the α-dioxime, causing a greater delocalization of the electrons in the 3d orbitals of the iron. This will weaken the shielding of s-electrons by 3d-electrons and decrease the isomer shift. Pyridine has a stronger π-accepting capability, while imidazole has a stronger σ-donor power. Both the effects by the axial ligands will decrease the isomer shift. Thus, the isomer shift of the complexes with the same α-dioxime may be changed little by the axial ligands.

Quadrupole Splitting. For metal-organic complexes, the electric-field gradient consists of both terms of the valence electrons of the Mössbauer nucleus and the ligands.[3] The electronic distribution of a ferrous ion in a strong crystal field has a cubic symmetry. Thus, octahedral low-spin iron(II) complexes show a single absorption peak or a doublet exhibiting a small quadrupole splitting.

The present complexes have a low-spin d^6 electronic configuration, while their observed quadrupole splittings are relatively large, especially in the pyridine adducts. Recently the Mössbauer spectrum of $\mathrm{Fe(II)(CdH)_2Im_2}$ was measured in the magnetic field.[4] The results indicate that the asymmetry parameter for this complex is quite large. On the other hand, the quadrupole splitting of the complexes containing CO or $\mathrm{CN^-}$ as axial ligands is normally small.[5] These findings suggest that we should consider the effects of π bonding on the axial ligands. According to the X-ray analyses of $\mathrm{Fe(II)(CdH)_2Im_2}$ and $\mathrm{Fe(II)(DgH)_2Im_2}$,[6,7] the π rings of imidazole are coplanar and are perpendicular to the hydrogen bond. The structure of these complexes is shown in Fig. 2. We assume that the central iron is in a nearly D_{2h} symmetry. Then, the π orbitals of the axial ligands may interact with only the 3d(xz) orbital. As pyridine has a stronger π-accepting capability than imidazole, the electrons in the 3d(xz) orbital of pyridine adducts will migrate more to the axial ligands. Thus, this may give a larger quadrupole splitting in pyridine complexes.

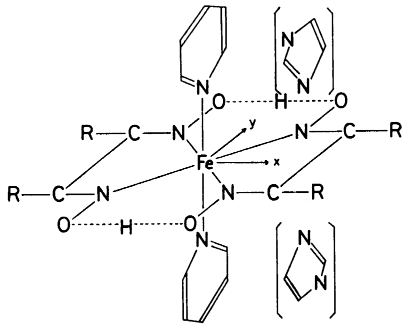

Fig. 2. The structure of the complex $\mathrm{Fe(II)(\alpha\text{-}dioxime)_2X_2}$.
(X=pyridine or imidazole)

The quadrupole splitting of the pyridine adducts increases in the order of: $\mathrm{CdH_2}$, $\mathrm{DgH_2}$, $\mathrm{FrH_2}$, and $\mathrm{BzH_2}$; the isomer shift decreases in the same order. In the imidazole complexes, $\mathrm{CdH_2}$ and $\mathrm{DgH_2}$ change places with each other.

An additional characteristic of the Mössbauer spectra of $\mathrm{Fe(II)(FrH)_2Py_2}$, $\mathrm{Fe(II)(BzH)_2Py_2}$, and $\mathrm{Fe(II)(FrH)_2Im_2}$ is found in the differences in the peak intensities of the doublet lines. Such an asymmetry can be ascribed to (1) crystal orientation,[8] (2) anisotropic recoilless fraction,[9,10] or (3) relaxation phenomena.[11] Because these complexes are diamagnetic, relaxation phenomena are not taken into account. As the samples were finely powdered, any effects due to crystal orientation would be eliminated. The temperature dependency of the Mössbauer spectra predicts, then, that there is an anisotropic recoilless fraction in these complexes.

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