Correlation of ^{57}Fe Mössbauer Spectra and Molecular Structure for an Iron(II) Complex with Inosine 5′-Monophosphate

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Received January 10, 1984

Despite the recent rapid growth in X-ray structural information about the binding of metal ions to nucleic acids and their components [1–3], there are numerous cases where structural conclusions must be based on less direct methods, usually because suitable crystals cannot be obtained. A notable example of this is provided by the iron derivatives of nucleotides. The early work of Rabinowitz and his coworkers [4] provided ^{57}Fe Mössbauer data for a range of iron(III) and iron(II) nucleotide complexes, but the reliability of structural conclusions drawn from these results was necessarily limited by the lack of X-ray information about any of the samples studied.

The recent isolation of $[Fe^{II}(5'\text{-IMP})(H_2O)_5]\cdot 2H_2O$ and determination of its crystal structure [5] showed the presence of three independent $[Fe(5'\text{-IMP})(H_2O)_5]$ molecules within the unit cell. The basic geometry about the iron atom is essentially the same in all three molecules; the metal is coordi-

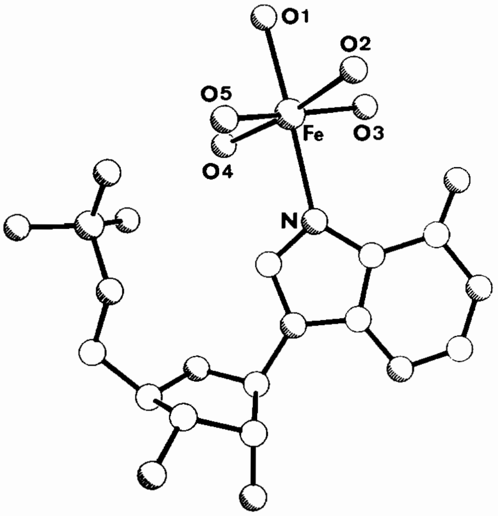

Fig. 1. Molecular structure of molecule II in $[Fe(5'\text{-IMP})(H_2O)_5]\cdot 2H_2O$ to show numbering scheme of atoms in the primary coordination sphere.

TABLE I. ^{57}Fe Mössbauer Parameters for $[Fe(5'\text{-IMP})(H_2O)_5]\cdot 2H_2O$.

T (K)		I.S.[a] (mm/s)	Q.S. (mm/s)	Γ[b] (mm/s)	Area (%)
4.2	A	1.365(14)[c]	3.059(14)	0.276(20)	35.2
	B	1.386(9)	2.598(9)	0.351(8)	64.8
80	A	1.341(2)	3.036(7)	0.280(3)	34.1
	B	1.362(1)	2.487(5)	0.390(3)	65.9
150	A	1.334(8)	2.935(8)	0.313(13)	36.4
	B	1.340(7)	2.248(7)	0.334(7)	63.6
250	A	1.260(12)	2.434(12)	0.341(18)	32.6
	B	1.281(6)	1.768(6)	0.352(8)	67.4
290	A + B	1.245(3)	1.691(3)	0.459(5)	–

[a] Relative to natural Fe. [b] Line width at half height. [c] Estimated error limits in brackets; *e.g.* (9) = ±0.009 mm/s.

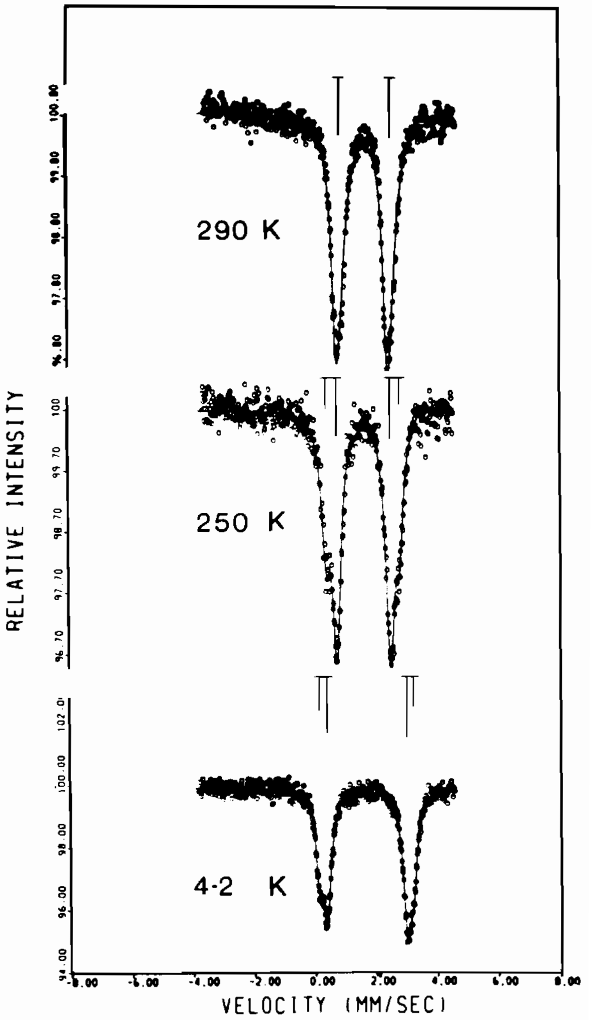

Fig. 2. ^{57}Mössbauer spectra of $[Fe(5'\text{-IMP})(H_2O)_5]\cdot 2H_2O$ at 4.2, 250 and 290 K.

0020-1693/84/$3.00

TABLE II. Bond Lengths (A) and Angles (°) in the Primary Coordination Sphere of [Fe(5'-IMP)(H_2O)$_5$]·$2H_2O$.

	Molecule I	Molecule II	Molecule III
Bond lengths	C3'-*endo*	C3'-*endo*	C2'-*endo*
Fe–O(1)	2.167	2.169	2.127
Fe–O(2)	2.121	2.133	2.098
Fe–O(3)	2.142	2.078	2.214
Fe–O(4)	2.106	2.077	2.097
Fe–O(5)	2.130	2.081	2.097
Fe–N	2.256	2.308	2.243
Bond Angles			
O(1)–Fe–O(2)	87.8	84.6	88.4
O(1)–Fe–O(3)	86.8	90.0	85.0
O(1)–Fe–O(4)	91.5	90.0	93.2
O(1)–Fe–O(5)	90.9	93.2	95.3
O(1)–Fe–N	176.4	174.2	176.2
O(2)–Fe–O(3)	88.8	86.0	90.6
O(2)–Fe–O(4)	175.9	171.7	173.9
O(2)–Fe–O(5)	92.7	80.8	96.7
O(2)–Fe–N	90.7	100.7	87.9
O(3)–Fe–O(4)	87.1	100.3	83.7
O(3)–Fe–O(5)	177.3	166.0	172.7
O(3)–Fe–N	96.5	88.1	94.0
O(4)–Fe–O(5)	91.4	93.3	89.0
O(4)–Fe–N	90.2	85.0	90.3
O(5)–Fe–N	85.8	89.9	86.2

nated to N(7) of the purine and to five water molecules which complete a distorted octahedron (Fig. 1). However, only two of the molecules (designated I and II) have the ribose ring C3'-*endo*, as commonly observed for other [M(5'-XMP)(H_2O)$_5$]·nH_2O (5'-XMP = purine 5'-monophosphate) structures; the third molecule, (III), has C2'-*endo*.

We have, therefore, studied the ^{57}Fe Mössbauer spectrum of this compound to see if these differences could be resolved in the spectra, and to provide reference data on a known system.

The spectra of a polycrystalline sample of [Fe(5'-IMP(H_2O)$_5$]·$2H_2O$, at various temperatures in the range 4.2–290 K are shown in Fig. 2. Those taken at $T \leqslant 250$ K comprise two overlapping quadrupole split doublets. The parameters derived for each doublet, denoted A and B, are given in Table I. The peak area ratios are consistent with an A:B ratio of 1:2 over the range 4.2–250 K.

The isomer shifts (I.S.) and the quadrupole splitting (Q.S.) values of both A and B are temperature dependent, and this is particularly true for the Q.S. values. The combined effects of these variations with temperature result in the overlap of the component peaks in the 290 K spectrum, which thus appears as a simple, but broadened, doublet.

The observation of spectra corresponding to the presence of two iron(II) sites in a 2:1 ratio might initially suggest a differentiation between those molecules in the unit cell with C3'-*endo* (I and II) and molecule III, which has the less common ribose conformation (C2'-*endo*). This is not, however, supported by an examination of the bond lengths and angles (Table II) [6] within each of the $FeNO_5$ coordination spheres. The iron atom in molecule II lies in a more distorted ligand field environment than those in I or III. The average of the Fe–O(2), Fe–O(3), Fe–O(4), and Fe–O(5) bond lengths, forming the (nominal) in-plane field, is significantly smaller for II (av. 2.092 Å) than for I (av. 2.125 Å) or III (av. 2.127 Å). Moreover the Fe–N bond in II is distinctly longer than in I or III, and this is not offset by any concomitant shortening of Fe–O(1). Molecule II also has some appreciable differences in bond angles compared with the analogous angles in I and III (see Table I). The combined effect is to produce a greater distortion of the octahedron of donor atoms about Fe in II than in I or III.

The structural information is consistent with assignment of the A bands in the Mössbauer spectra to Fe site II (greater Q.S. value at a given temperature), and the more intense bands of doublet B to both sites I and III.

The general range of the I.S. and Q.S. values are as expected [7] for the known high-spin electronic configuration (μ 5.38 B.M. [5]) of the iron atoms. The temperature dependence of Q.S. for both doublets and, particularly, the large values at low temperature indicate an orbital singlet ground state [8], with a greater splitting of the original t_{2g} orbital set for 11 than for I and III. This is consistent with the low site symmetry, C_1, observed for all the iron atoms in the structural study. In such low symmetry, derivation of accurate ligand field distortion parameters from powder Mössbauer spectra is open to question [8], but a rough estimate may be made of the primary (axial) distortion, which has the major influence on the temperature dependence of Q.S. [8]. Approximate derived values of δt_{2g} of *ca.* 400–500 cm^{-1} for II and 200–300 cm^{-1} for I and III seem reasonable from the observed geometries and the (averaged) orbital contribution to the magnetic moment [9].

Rabinowitz and co-workers reported [4] Q.S. values of 2.90–3.10 mm/s and I.S. values (after conversion to mid-point of Fe as reference) of 1.27–1.35 mm/s at 77 K for samples describing as lyophilized powders of Fe(II)–ATP, Fe(II)–ADP, and Fe(II)–AMP. These results, particularly the Q.S. values, correspond to those of the more distorted iron(II) site in [Fe(5'-IMP)(H_2O)$_5$]·$2H_2O$. However no analytical data were given for their samples, so the extent of hydration is unknown.

Experimental

The compound was prepared as described previously [5]. Details of the Mössbauer spectrometer have been discussed by Woodhams *et al.* [10]. Curve fitting was provided by the programme MAGPLT, a derivative of the N.B.S. programme MADG [11]. The radiation source was ^{57}Co (nominally 25 mCi, Radiochemical centre) in a 6 μm rhodium matrix, calibration standard was 25 μm natural iron foil (Radiochemical centre).

Acknowledgements

We thank the S.E.R.C. and Imperial Chemical Industries PLC for a CASE Studentship to P.B.H.

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