MEASUREMENT OF NUCLEAR QUADRUPOLE INTERACTION IN IRON COMPLEXES USING THE MOSSBAUER EFFECT

by

Neyla L. Costa, J. Danon, R. Moreira Xavier

MEASUREMENT OF NUCLEAR QUADRUPOLE INTERACTION IN
IRON COMPLEXES USING   THE MOSSBAUER EFFECT *

Neyla L. Costa,   J. Danon, R. Moreira Xavier
Centro Brasileiro de Pesquisas Físicas
Rio de Janeiro, Brasil

The field gradient at the Fe^{57} nucleus in strongly dependent on the d electrons. Quadrupole coupling measurements of the Mossbauer effect with Fe in different electronic surroundings should give infor- mation concerning the distribution of these electrons.

The measurements of the Mossbauer effect were made with a source of Co^{57} diffused into stainless steel and emitting an unsplitted monochromatic 14.4 kev line. The method of   measurement and the technique for inducing Doppler shift of the emission line were the same as   those   used by Kistner and Sunyar[1].   Fourteen different

iron complexes, in the bivalent and trivalent state, of the spin-free and spin-paired type, were investigated as absorbers. Besides potassium ferrocyanide, potassium ferricyanide, and sodium nitroprusside which are commercially available salts, the substituted cyanides were prepared according to Hoffman[2], $\left[Fe^{III} F_5(H_2O)\right]K_2$ and the oxalate complexes according to Palmer[3], $\left[Fe^{III} F_6\right]K_3$ according to Peacock[4] and $\left[Fe^{III} Cl_5(H_2O)\right](N H_4)_2$ according to Lindqvist[5].

The results obtained are given in table I. ΔE is the quadrupole splitting and δ is the isomer shift, both in cm/sec as defined by DeBenedetti[6]. The experiments have been performed at romm temperature.

Under the influence of a field with almost cubic symmetry the 5 d orbitals of iron split into a doublet d_γ and a triplet d_ε of lower energy[7, 8, 9].

In the weak field coupling scheme the ground state has always the highest possible multiplicity. The electron configuration of these so-called spin-free or "ionic" complexes are $d_\varepsilon^4 d_\gamma^2$ for Fe^{++} and $d_\varepsilon^3 d_\gamma^2$ for Fe^{+++}. In the strong field coupling scheme the electron configuration d_ε^6 for Fe^{++} and d_ε^5 for Fe^{+++} form the so-called spin-paired of "covalent" complexes, as obtained with the iron cyanides.

Since $d_\varepsilon^3 d_\gamma^2$ and d_ε^6 possess spherical and cubic symmetry respectively there is no contribution from the inner electron configuration to the field gradient at the nucleus. The cubic symmetry of the octahedral disposition of the six ligands around the iron atom also does not give any contribution to the field gradient. This ex-

plains why no quadrupole splitting is observed with spin-free complexes of Fe^{+++} such as $\left[Fe^{III}F_6\right]^{+3}$ and spin-paired complexes of Fe^{++} such as $\left[Fe^{II}(CN)_6\right]^{+4}$.

Deviations from the cubic symmetry can be obtained by forming FeX_5Y complexes such as $\left[Fe^{III}F_5(H_2O)\right]^{+2}$ and $\left[Fe^{II}(CN)_5(H_2O)\right]^{+3}$. The three d_ϵ levels become more or less separated according to the degree of distortion from the cubic symmetry. However, since this may not change significantly the spherical symmetry of the inner electronic configuration a relatively low quadrupole splitting is observed with these complexes. A possible exception is the nitro prusside complex which will be considered later.

With $\left[Fe^{III}Cl_5(H_2O)\right]^{+2}$ no splitting was obtained although the crystal structure data definitely excludes the possibility of cubic symmetry around the iron atom[5]. However, the relatively large width of the resonance curve suggests that the quadrupole interaction occurs and that the value of the splitting is below the resolving power of our apparatus.

Spin-free Fe^{++} has an extra d_ϵ electron while spin-paired Fe^{+++} has a hole in the complete d_ϵ shell. The contribution of these configurations to the field gradient depend on the symmetry of the external field and on the temperature. In almost cubic surrounding the three d_ϵ levels should be close in energy. At $T = 0°K$ the above configurations should give exactly the same quadrupole splitting. As a function of temperature the quadrupole splitting should decrease. This decrease is rapid if the three d_ϵ levels are close in energy, slow if they are widely separated. It may happen

that at room temperature the three d_ϵ states of $\left[Fe^{III}(CN)_6\right]^{+3}$ mix more rapidly than 10^{-7} sec (half-life of Fe^{57m}). The nucleus would then observe the average field which has spherical symmetry because the three d_ϵ states are equally populated. This would explain the absence of splitting in this complex. On the other hand the mixing of these states seems not to occur with spin-free Fe^{II} complexes where the splitting is maintained at room temperature[6].

In the distorted cubic symmetry, as with $\left[Fe^{III} X_5 Y\right]$ complexes, the three d_ϵ levels are widely separated in energy. No mixing of the states occur at room temperature and the quadrupole splitting results from the assymetry of the inner electron configuration and that of the distorted immediate surroundings.

The chemical properties of $\left[Fe (CN)_5 NO\right]^{+2}$ are those of a trivalent iron cyanide. However, this complex is diamagnetic and this is explained by assuming that one electron from the NO is transfered to the central iron atom. The inner d_ϵ shell should thus be closed with six paired electrons as in a spin-paired Fe^{++} complex and the NO ligand becomes positively charged. It is interesting to observe that the quadrupole interaction for this complex is of the same order of magnitude as that obtained with the substituted spin-paired Fe^{+++} complexes, as if no transfer of electron had occured. The isomer shift obtained for this complex does not fall in any of the group of values of the other iron complexes.

The data on the isomer shift indicate that the electron density at the nucleus is smallest in spin-free Fe^{++}, and progressively increases in spin-free Fe^{+++}, spin-paired Fe^{++} and spin-

-paired Fe^{+++}. This shows that the electron of the ligands must be closer to the iron nucleus in the spin-paired case in order to increase the separation between the d_ϵ and the d_γ orbitals.

Acknowledgements

* * *

References

1. O. C. Kistner and A. W. Sunyar - Phys. Rev. Letters, 4, 412 (1960).
2. K. A. Hofmann, Ann. Chem. 312, 1 (1900).
3. W. G. Palmer, Experimental Inorganic Chemistry, Cambridge University Press, 1954, pg. 519.
4. R. D. Peacock, J. Chem. Soc. 4684 (1957).
5. I. Lindqvist, Ark. Kemi Mineralog. Geol. 24, 1 (1946).
6. S. DeBenedetti, G. Lang e R. Ingalls, Phys. Rev. Letters 6, 60 (1961).
7. R. S. Nyholm, Rapports et Discussions du Xe Conseil de Chimie, Université de Bruxelles, 1956, pg. 225.
8. R. J. Gillespie e R. S. Nyholm, Quartely Reviews of Chem. Soc. 11, 331 (1957).
9. L. E. Orgel - "Transition Metal Chemistry - METHUEN CO., London (1961).

TABLE I. Quadrupole splittings ΔE and chemical shifts δ at room temperature for iron complexes.

KIND OF COMPLEX ION	ABSORBER	ΔE(cm/sec)	δ(cm/sec)
Spin-paired Fe^{II}	$[Fe(CN)_6]K_4 \cdot 3H_2O$	0.000 ± 0.005	0.008 ± 0.005
	$[Fe(CN)_5H_2O]Na_3 \cdot 7H_2O$	0.080 ± 0.005	0.015 ± 0.005
	$[Fe(CN)_5NO_2]Na_4$	0.089 ± 0.005	0.010 ± 0.005
	$[Fe(CN)_5NH_3]Na_3 \cdot 6H_2O$	0.070 ± 0.005	0.019 ± 0.005
	$[Fe(CN)_5SO_3]Na_5 \cdot 9H_2O$	0.080 ± 0.005	0.010 ± 0.005
	$[Fe(CN)_5NO]Na_2 \cdot 2H_2O$	0.185 ± 0.005	-0.012 ± 0.005
Spin-free Fe^{III}	K_3FeF_6	0.000 ± 0.005	0.055 ± 0.005
	$[FeCl_5H_2O](NH_4)_2$	0.000 ± 0.005	0.060 ± 0.005
	$[FeF_5H_2O]K_2$	0.040 ± 0.005	0.054 ± 0.005
Spin-free Fe^{II}	$FeC_2O_4 \cdot 2H_2O$	0.178 ± 0.005	0.136 ± 0.005
Spin-paired Fe^{III}	$[Fe(CN)_6]K_3$	0.000 ± 0.005	0.000 ± 0.005
	$[Fe(CN)_5H_2O]Na_2$	0.182 ± 0.005	0.000 ± 0.005
	$[Fe(CN)_5NH_3]Na_2 \cdot H_2O$	0.178 ± 0.005	0.000 ± 0.005
	$[Fe(CN)_5NO_2]Na_3$	0.178 ± 0.005	0.000 ± 0.005