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MOLECULAR STRUCTURE INVESTIGATIONS
WITH THE MÖSSBAUER EFFECT

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MOLECULAR STRUCTURE INVESTIGATIONS WITH THE MÖSSBAUER EFFECT *

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1. Nuclear Isomer Shift and the Nephelauxetic Effect in Iron Complexes

The nephelauxetic effect (N.E.) is the decrease of the parameters of interelectronic repulsion in transition ion complexes compared with the corresponding gaseous ion ¹. This decrease corresponds to an expanded radial function of the partly filled shell.

The contributions to the isomer shift in iron comes from:
a) electrons in the filled 1s, 2s and 3s shells and the partial occupation of the 4s orbitals by electrons from the ligands ². The

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partial occupation of the 4s orbitals contribute to the N.E. through the shielding of the central field (central field covalency) ¹; b) the decrease in the shielding of s-electrons due to the delocalization of d-electrons in molecular orbitals. This spread of d-electrons contribute to the N.E. through the restricted symmetry covalency ¹.

The nephelauxetic series of ligands usually corresponds to their increasing polarizability, decreasing electronegativity and increasing tendency to covalent bond formation: F^- , H_2O , NH_3 , Cl^- , CN^- , Br^- , S. It has been pointed out that with Fe^{+2} the order of decreasing isomer shift (I.S.), $O > S > Se > Te$, is that of decreasing ligand electronegativity ³. Careful measurements with iron complexes ⁴ show that the order of decreasing I.S. is essentially the same as that of the polarizability of the ligands: $H_2O \sim Acet. > Citrate \sim PO_4 > OH \sim NO_3$. With octahedral high-spin Fe^{+3} complexes we observed the decreasing I. S.: $F > H_2O > Cl > Br$. We recall that decreasing I.S. means increasing s-electron density.

A calibration of the observed I.S. in terms of total s-electron density has been made by assuming a negligible occupation of the 4s orbitals in iron complexes with F, H_2O ². However, even in the more ionic Fe^{+3} complexes the N.E. is large. This may explain why the values of 4s density derived from that calibration are smaller than those calculated by charge transfer from effective electronegativity.

In spin-paired iron complexes such as with Cl the I. S. decreases with increasing electronegativity of the ligand ($CN^- > CO > NO^+$) which suggests an extensive π -bonding (back-donation) between the

Fe atom and the ligands⁵. In such cases the contribution of π -bonding to the I.S. (by decreasing s-electron shielding) appears so strong that it breaks the parallelism between I.S. and N.E. Thus, the I.S. is smaller with CN^- than with Br^- or S. The importance of π -bonding to the I.S. is suggested by the fact that the increase in s-density on going from high-spin Fe^{+2} to low-spin Fe^{+2} complexes is higher than the corresponding increase on going from Fe^{+2} to Fe^{+3} high-spin complexes. This shows that the decrease in s-electron shielding as a consequence of the delocalization of d-electrons in the π -bond is larger than that due to the removal of a d-electron from the iron atom.

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2. Studies on the Electronic Structure of Fe-NO Complexes by the Mossbauer Effect

The NO ligand has an unpaired electron that can expand in a M. O. formed with the d orbitals of a transition ion.

$\text{Fe}(\text{CN})_5\text{NO}^{-2}$ is a diamagnetic spin-paired complex of NO^+ . The nuclear quadrupole coupling $\Delta E = 0.185$ cm/sec was found to have the double value of that observed with other diamagnetic iron (II) pentacyanides ¹. The isomer shift $\sigma = -0.012$ cm/sec indicates one of the largest s-electron density observed with iron complexes. Comparison between these values and those obtained with other $\text{Fe}(\text{CN})_5\text{Y}$ complexes shows the order $\text{FeNO} > \text{Fe}^{+3} > \text{Fe}^{+2}$. The Fe ion in the NO bonded complex appears as having a formal charge more positive than +3. Infra-red measurement in the region of the Fe-CN stretching leads to the same conclusion ². These facts can be interpreted by assuming that in $\text{Fe}(\text{CN})_5\text{NO}^{-2}$ the unpaired d electron of low-spin Fe^{+3} couples with the unpaired electron of NO, both electrons being delocalized in a strong π -bond. Evidence for delocalization from NO is given by infra-red spectra (NO^+) and by analogy from measurements from EPR in $\text{Cr}(\text{CN})_5\text{NO}^{-3}$ which show a decreased hyperfine interaction with the N nucleus ³. Delocalization of the d electron from the low-spin $3d^5$ configuration leads to a $3d^4$ configuration which explains the double value for the electric field gradient at the Fe_{57} nucleus observed. This delocalization will decrease the shielding of the s-electrons and this explains the large s-electron density observed ⁴.

It has been suggested that the strong M-NO π -bonds dominate the overall electronic structure of these complexes and determines the relative energies of the metal d orbitals ⁵. A.M.O. scheme derived from this rule allowed an interpretation of the I.R., optical and EPR results for $\text{Fe}(\text{NO})[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$ ⁶. The lower s-density observed with this complex ($\sigma = +0.038$ cm/sec) as compared with $\text{Fe}(\text{CN})_5\text{NO}^{-2}$ is consistent with the expansion of the unpaired electron from NO in an empty antibonding d orbital of spin-paired Fe^{+2} which increases the d-electron density and the shielding of the s-electrons. The value for $\Delta E = 0.085$ cm/sec is the same as those obtained with low-spin $\text{Fe}^{\text{II}}(\text{CN})_5\text{Y}$ complexes suggesting, as expected, that the increase in d-electron density is not enough to alter the quadrupole interaction.

$\text{Fe}(\text{H}_2\text{O})_5\text{NO}^{+2}$ is a high-spin Fe^{+2} complex of NO^+ . We observed $\Delta E = 0.170$ cm/sec and $\sigma = +0.140$ cm/sec as expected for Fe^{+2} in such configuration with some covalent character. Although the unpaired electron of NO is coupled with a d-electron of Fe, the delocalization of both is small. Further studies are necessary for an understanding of the electronic structure of these Fe-NO aquo complexes.

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3. Mossbauer Effect with Trivalent Iron Halides in Different Molecular Symmetries

The nuclear quadrupole interaction ΔE with the 6S_5 state of Fe^{+3}_{57} is usually low, since no contribution is expected from inner electron shells to the electric field gradient at the iron nucleus. The observed quadrupole coupling are related to the degree of distortion from cubic symmetry of the ligand field.

Essentially no quadrupole coupling was observed with octahedral FeF_6^{-3} , $FeCl_3$ and $FeBr_3$. The isomer shift σ decreases from + 0.055, + 0.045 to + 0.030 cm/sec with decreasing electronegativity of the halogens.

With $FeF_5(H_2O)^{-1}$ at room temperature $\Delta E = 0.055$ cm/sec. No interaction was observed with $FeCl_5(H_2O)^{-1}$ at room temperature and a small one ($\Delta E = 0.023$) at liquid nitrogen temperature. From ionic radius and electronegativity considerations one should expect less departure from the cubic symmetry when Cl^- instead of F^- is substituted by H_2O .

With tetrahedral $FeCl_4^{-1}$ $\Delta E = 0.030$ and $\sigma = + 0.040$ cm/sec; approximately the same values were obtained with Fe^{+3} in tetrahedral yttrium iron garnet ¹.

With $FeF_3 \cdot 4.5H_2O$ and $FeF_3 \cdot 3H_2O$ we observed the same values $E = 0.055$ and $\sigma = + 0.055$ cm/sec. $FeCl_3 \cdot 6H_2O$ gives an unusually large interaction ($\Delta E = 0.10$ cm/sec); the intensity is different in the two peaks ² and the usual Fe^{+3} isomer shift was

observed ($\sigma = + 0.050$ cm/sec). Nearly the same values were found at room and liquid N_2 temperatures.

The structure of the Fe^{+3} hydrated halides is unknown, but probably is not similar to that of $AlCl_3 \cdot 6H_2O$ or $CrCl_3 \cdot 6H_2O$. In these the six H_2O form a nearly regular octahedron. The small ΔE observed with $Al_{27}Cl_3 \cdot 6H_2O$ ³ can be due to the field of the Cl ions which are placed with low symmetry as second neighbours⁴. With $AlCl_3 \cdot 6H_2O$ grown from a solution containing Fe_{57} the Mossbauer effect shows that the field gradient at the Fe_{57} sites is much larger than at Al sites³. This is probably not due to the distortion of the lattice³ as a consequence of the difference in ionic radius between Fe^{+3} and Al^{+3} , since nearly the same ΔE is found with the substituted Fe^{+3} and the pure $FeCl_3 \cdot 6H_2O$. Distortions of the S state of Fe^{+3} by the crystal field are second order effects and cannot account for the difference in ΔE between Fe and Al. Moreover, with $FeCl_3 \cdot 6NH_3$ which is expected to have the same cubic YF_3 structure of $AlCl_3 \cdot 6NH_3$ ⁴ we observed a relatively large interaction ($\Delta E = 0.055$).

We believe that in Fe^{+3} hydrated halides (and amines) some of the halogens, if not all, are directly bonded to the iron atom forming a low symmetry structure. Some interesting properties of these compounds can be interpreted on the basis of such a structure. It has recently been shown that in $GdCl_3 \cdot 6H_2O$, besides the six H_2O , two Cl^- approach the central ion and the resulting structure is like $[GdCl_2(H_2O)_6]Cl$ ⁵.

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