Mössbauer Results for some Low-spin Iron(IV) Compounds

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Summary Mössbauer data for the *trans*-$[Fe(das)_2X_2][BF_4]_2$ complexes indicate a ground state configuration of $d^2_{xy}d_{xz}d_{yz}$.

THE most common oxidation states of iron are Fe^{II} and Fe^{III} although there are scattered reports[1–3] of both high and low spin Fe^{IV} complexes. Examples of the latter include some molecules of biological significance such as the complex ES derived from cytochrome c peroxidase[1] and a derivative of horseradish peroxidase.[2] From magnetic susceptibility, spectral, and conductivity measurements Hazeldean, Nyholm, and Parish[3] concluded that the complexes, *trans*-$[Fe(das)_2X_2][BF_4]_2$ where (das) = *o*-phenylenebis(dimethylarsine) and X = Cl and Br, contained spin-paired Fe^{IV} with a d_ε^4 configuration. We report Mössbauer data for these compounds.

Mössbauer effect parameters for trans-$[Fe(das)_2X_2][BF_4]_2$ *complexes*

Compound	Temperature	ΔE (mm/sec.)	C.S. (mm/sec.)*	% Effect
trans-$[Fe(das)_2Br_2][BF_4]_2$	298 K	3·16 ± 0·05	0·17 ± 0·05	1·42 ± 0·3
	78	3·19 ± 0·05	0·25 ± 0·05	3·76 ± 0·3
	20	3·20 ± 0·05	0·26 ± 0·05	4·62 ± 0·3
	4·2	3·25 ± 0·05	0·27 ± 0·05	4·42 ± 0·3
trans-$[Fe(das)_2Cl_2][BF_4]_2$	348	3·07 ± 0·05	0·08 ± 0·05	——
	298	3·22 ± 0·05	0·12 ± 0·05	6·53 ± 0·5
	78	3·30 ± 0·05	0·20 ± 0·05	13·48 ± 0·5
	20	3·23 ± 0·05	0·20 ± 0·05	14·00 ± 0·5
	4·2	3·22 ± 0·05	0·20 ± 0·05	16·76 ± 0·5

* With respect to metallic iron.

The sample was prepared[3] with iron enriched to about 90% ^{57}Fe and mixed with inert boron nitride powder to provide an even distribution of compound over the sample holder. Sample preparation and Mössbauer measurements were carried out in an inert atmosphere to prevent conversion of *trans*-[Fe(das)$_2$X$_2$] [BF$_4$]$_2$ to *trans*-[Fe(das)$_2$X$_2$] [BF$_4$]. Mössbauer data for the Fe^{III} complex will be reported elsewhere. The experimental data (Figure, Table) were normalized, corrected for solid angle effects, and fitted by a least-square procedure to Lorentzian line shapes to determine the position, intensity, and width of each peak.

From the Table it can be seen that the temperature dependence of the centre shifts are within the variation expected from the second-order Doppler effect. The values of the centre shifts are in agreement with those found for other Fe^{IV} materials and are comparable to those determined for low-spin Fe^{II} and Fe^{III} compounds such as ferro- and ferricyanides.[4] It appears that $|\psi(0)|^2$ is similar in all of these low-spin complexes. Moreover, the centre shift of the chloro-derivative is slightly less positive than that of the bromo-complex. These relative values agree with the correlation of centre shift with the spectrochemical series of ligands found for a large number of low-spin Fe^{II} complexes.[5]

The quadrupole splitting $\Delta E = e^2Qq/2$ is about 3·2 mm/sec. for both compounds and is independent of temperature over the range from 4·2K to 300K. The sign of the electric field gradient was determined to be positive in an external field of 50 kG. for the chloride complex. These data are consistent with D_{4h} symmetry for the *trans*-[Fe(das)$_2$X$_2$]$^{2+}$ cation in which the two halogen ligands are in apical positions. A strong axial crystal field which separates the excited orbitals by at least 300K from the ground state is suggested by the temperature independence of the quadrupole splitting.

The major contribution to the electric field gradient q is due to the valence d-electrons and the expression for q is:

$$q = [4/7(n_{xy}) - 2/7(n_{xz} + n_{yz})] < r^{-3} >$$

where n is the electron population in the various iron d_ε orbitals. Under the assumption of D_{4h} symmetry, the axial ligand field will remove the degeneracy of the $^3T_{1g}(O_h)$ state to give the levels $^3A_{2g} + {}^3E_g$. The positive value of q determined in an external magnetic field indicates that the ground state is $^3A_{2g}$ corresponding to a $d^2_{xy}d_{xz}d_{yz}$ configuration. This $^3A_{2g}$ ground state is a result of the strong axial ligand field created by the halogen atoms.

The experimental values determined for the quadrupole splitting show q *ca.* 4/7 $<r^{-3}>$. This value is somewhat greater than expected if there were a large amount of electron delocalization from the iron atom into the ligand orbitals. This suggests that any back π-donation which occurs from the iron atom to the four planar arsenic atom orbitals may be offset by concomitant π-donation from the two axial halogen atoms. The small amount of electron delocalization from the iron atom is consistent with the high formal positive charge of iron in the *trans*-[Fe(das)$_2$X$_2$]$^{2+}$ cation.

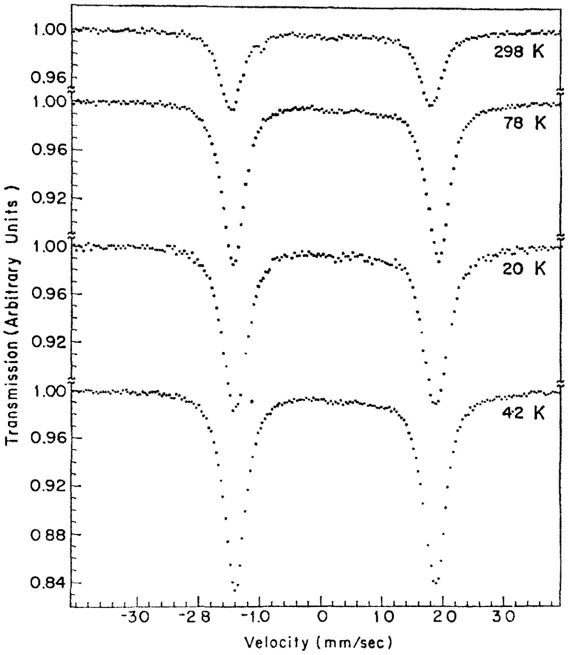

FIGURE. *Mössbauer spectra of powdered* trans-[Fe(das)$_2$Cl$_2$]-[BF$_4$]$_2$. *The zero of the velocity scale is the centre of the spectrum of metallic iron at room temperature.*

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