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Compounds with Extremely Negative Mössbauer-Effect Isomer Shifts: A Probe of Intermetallic Bonding in $Zr_6Cl_{14}Fe$, $LiZr_6Cl_{15}Fe$, and $KZr_6Cl_{15}Fe$

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Chemists, materials scientists, and Mössbauer spectroscopists have long used the iron-57 isomer shift as an important method for characterizing compounds' oxidation states.[1,2] Indeed, Danon and co-workers[3] demonstrated a nice linear correlation[4] between the isomer shift, the iron 3s- and 4s-electron densities at the nucleus, and the iron oxidation state. This correlation included the 295 K iron(VI) isomer shift of ca. −0.89 mm/s, relative to α-iron, obtained[5−7] for K_2FeO_4, $SrFeO_4$, and $BaFeO_4$. To our knowledge, these are the most negative iron-57 isomer shifts that had ever been reported in an iron compound. However, other notable examples include values[8,9] of ca. −0.75 mm/s, reported for a variety of rare gas matrix isolated iron atoms, and a value of −0.55 mm/s, reported for $Ba_3(FeN_3)$, for which a local spin-density functional ASW calculation yielded $3d^{5.83}4s^{0.44}4p^{0.58}$ partial charges in the Fe sphere.[10] To our surprise, we have obtained 295 K isomer shifts for compounds containing Fe-centered hexanuclear zirconium chloride clusters that were even more negative than −0.95 mm/s. The extremely negative isomer shifts reported in this paper demonstrate that the association of negative isomer shifts with high iron oxidation states is not universal and that such correlations must be made with care.

The chemistry of Zr_6Cl_{12}-based clusters containing an interstitial atom such as iron has been extensively studied, both in solution[11,12] and solid state.[13−16] In these clusters, twelve chlorine atoms are always bonded to the edges of the Zr_6 octahedron and six additional chlorine atoms are on the terminal positions that radiate from each apex of the octahedron. These terminal chlorine atoms are shared between clusters in the solid state such that the M^I-$Zr_6Cl_{15}Fe$ (M^I = Li or K) are usefully formulated as $M^I[(Zr_6FeCl_{12})Cl_{6/2}]$,[16] where 6/2 signifies six terminal chlorine atoms per cluster that shared between two neighboring Zr_6FeCl_{12} clusters (Figure 1). In $Zr_6Cl_{14}Fe$ some chlorine atoms are shared more intimately between clusters and some edge-bonded chlorine atoms serve as terminal ligands on neighboring clusters. The iron atoms in the Zr_6FeCl_{12} clusters reside in a nearly octahedral environment, but perfect octahedral symmetry is inconsistent with the space group symmetry. Thus, the detailed structure of $KZr_6Cl_{15}Fe$ is such that there are two very slightly different Fe atom sites, each with only C_s symmtery.[14−16] It should be noted that, in the various iron-containing Zr_6Cl_{12}-based cluster compounds, the six zirconium−iron bond distances are ca. 2.43 Å, a value that is much smaller than the 2.64 Å sum of the single bond radii. Substantial covalency in the Zr−Fe bonds is implied by the shortness of these bonds and was discussed in a previous molecular orbital treatment.[17]

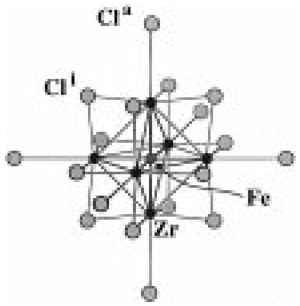

Figure 1. The structure of an Fe-centered cluster in $KZr_6Cl_{15}Fe$. Terminal chlorides (Cl^a) are shared between adjacent clusters in the solid state.

The compounds were prepared as described elsewhere.[11,15,16,18−20] The 78 K Mössbauer spectrum of $KZr_6Cl_{15}Fe$ is shown in Figure 2 and the Mössbauer spectral parameters for all three compounds are given in Table 1. The remaining Mössbauer spectra are very similar to that shown in Figure 1 except that they exhibit less resolution of the quadrupole doublet. As expected from the nearly octahedral environment of the iron,[21] all of the quadrupole splittings, ΔE_Q, are small and, with the exception of $KZr_6Cl_{15}Fe$, are virtually independent of temperature. The change in ΔE_Q with temperature observed for $KZr_6Cl_{15}Fe$ is reproducible, and may be associated with an anisotropic contraction of the crystal upon cooling.

By measuring the temperature dependence of the Mössbauer spectral isomer shifts and absorption areas, the effective recoil mass, M_{eff}, and the effective Mössbauer temperature, Θ_D, of iron-containing compounds can be determined.[22] The effective recoil mass is a measure of the covalency of the iron bonding, whereas

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(18) These compounds are air and moisture sensitive and all sample manipulations, absorber preparations, and spectral measurements were carried out under an inert atmosphere or under vacuum.

(19) Mössbauer spectra were obtained at 78 and 295 K on a constant-acceleration spectrometer which utilized a room temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with α-iron foil. Absorber thicknesses were ca. 98 mg/cm^2 and the resulting spectra have been fit with a symmetric quadrupole doublet.

(20) Earlier studies indicate that the isomer shifts, quadrupole splittings, and line widths are reproducible to ±0.004, ±0.02, and ±0.01 mm/s, respectively, and that the spectral absorption areas are reproducible to ±0.5%. The effective recoil masses are valid to ca. ±10 g/mol and the effective Mössbauer temperatures are valid to ca. ±15 K.

(21) The iron atom in $LiZr_6Cl_{15}Fe$ resides in a site of crystallographic cubic symmetry, but disorder in the lithium ion positioning will reduce the true local symmetry.

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Table 1. Mössbauer Spectral Hyperfine Parameters

compd	T, K	δ, mm/s[a]	ΔE_Q, mm/s	Γ, mm/s	M_{eff}, g/mol	Θ_D, K
$Zr_6Cl_{14}Fe$	295	−0.946	0.09	0.27	125	242
	78	−0.874	0.12	0.24		
$LiZr_6Cl_{15}Fe$	295	−0.937	0.10	0.25	120	295
	78	−0.862	0.11	0.24		
$KZr_6Cl_{15}Fe$	295	−0.953	0.14	0.25	138	163
	78	−0.888	0.30	0.27		

[a] Isomer shifts are reported relative to room temperature α-iron foil.

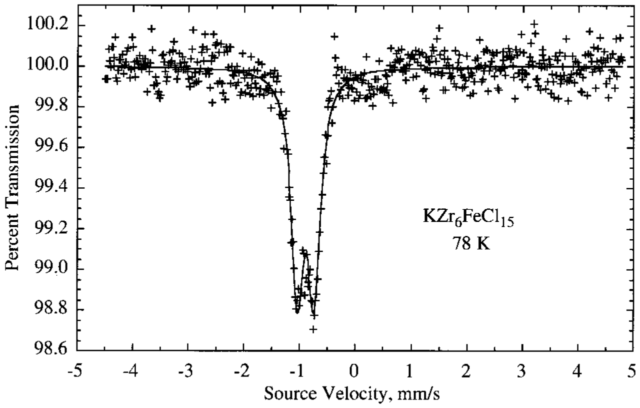

Figure 2. The Mössbauer effect spectrum of $KZr_6Cl_{15}Fe$ obtained at 78 K.

the effective Mössbauer temperature is equivalent to the Debye temperature of an elemental solid. The resulting values, given in Table 1, are very reasonable, but because the values are based on only two data points it is not certain that the values for $KZr_6Cl_{15}Fe$ are significantly different from those of the other two compounds. The observed values for M_{eff} are consistent with extensive covalent bonding of iron within the Zr_6Fe cluster.[17]

The most unusual and interesting aspect of all the spectra is the very negative isomer shift, δ. The isomer shift is known[1−3] to decrease as the s-electron density at the iron-57 nucleus increases. An increase in the electron density at the Fe nucleus can occur directly as a result of an increased 4s-orbital population, or by a relative deshielding of both the 3s and 4s electrons by a decrease in the population of intervening 3d-orbitals. The second factor seems to be an especially important influence on the very negative isomer shifts of high oxidation state compounds such as the iron(VI) oxides.[3] Deshielding may contribute significantly to the high s-electron density in $Ba_3(FeN_3)$.[10] However, it is clearly unreasonable to assign a high formal oxidation state to an iron center that is imbedded within a zirconium cage, and the Fe 3d population in Zr_6FeCl_{12}-based clusters is expected to be relatively high.[17]

An approximate idea of the "4s-electron density" at the iron-57 nucleus may be obtained from the Walker−Wertheim−Jaccarino diagram,[23] which provides a family of curves that correlate the isomer shift to the iron 4s orbital population; the effect of differential 3s-electron screening is accounted for by constructing different curves for each formal 3d electron count (the lower the 3d-count, the more negative the isomer shift). The diagram allows an estimate of ca. 78 electrons/Å^3 for the iron electronic density at the nucleus, which is much higher than the corresponding 66 electrons/Å^3 of α-iron. Assuming the iron 3d population for this cluster system is in the range between 6.0 and 7.0, the respective bounds on the 4s orbital population would be between 0.9 and 1.7 electrons.

We have performed density functional theory (DFT) electronic structure calculations to obtain s-electron densities. Electronic structure calculations on the solid $LiZr_6Cl_{15}Fe$ ($k = 0$ only) and two reference molecules, ferrocene and $Fe(CO)_5$, were performed with the Becke−Lee−Yang−Parr (BLYP) nonlocal exchange-correlation functional.[24−28] These computed 3d Mulliken populations for all three systems are quite comparable, but the iron 4s electron density is much higher for $LiZr_6Cl_{15}Fe$ than for the other two systems: $LiZr_6Cl_{15}Fe$, $3d^{6.92}4s^{0.92}$; ferrocene, $3d^{7.02}4s^{0.48}$; and $Fe(CO)_5$, $3d^{6.96}4s^{0.23}$. The corresponding 295 K isomer shifts are −0.937, 0.45, and −0.09 mm/s relative to α-iron.[29,30] The very similar Fe 3d populations of the two reference molecules are useful in demonstrating that a high 4s population need not arise from deshielding alone, even if the computed 4s populations do not correspond to the ordering of their isomer shifts.

The qualitative bonding picture derived from the DFT calculations on $LiZr_6Cl_{15}Fe$ is essentially identical to one previously derived from extended Hückel calculations.[17] The surrounding Zr_6Cl_{12} cage possesses an a_{1g} orbital that is composed of an in-phase combination of six zirconium $4d_{z^2}$ orbitals. This totally symmetric combination overlaps with the iron 4s orbital to form a bonding MO that is the most stable of nine occupied Zr_6Fe-localized MOs. The a_{1g}-symmetry Zr_6Cl_{12} cage orbital with which the Fe 4s orbital mixes lies much higher in energy than the corresponding totally symmetric orbital formed from the σ-bonding lone pairs of conventional ligands. Consequently, the occupied bonding a_{1g} MO has much more iron 4s character than a corresponding orbital in a typical inorganic or organometallic complex, which are predominantly ligand centered. Fundamentally then, the very negative isomer shifts observed in these clusters are the result of the electropositive environment presented to an iron atom within a Zr_6 cage. The bonding in the structurally similar Th_6Fe cluster compounds has been discussed in similar terms.[31] Additional Mössbauer spectral measurements and a more comprehensive theoretical analysis will be undertaken to buttress these conclusions.

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