Quadrupole Splittings in the Mössbauer Spectra of $[Fe_4S_4(SBu^t)_4]^{2-}$ Salts

DAVID J. EVANS, G. JEFFERY LEIGH

AFRC-IPSR Nitrogen Fixation Laboratory at the University of Sussex, Brighton, BN1 9RQ, U.K.

ANDREW HOULTON and JACK SILVER

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, U.K.

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Mössbauer spectroscopy has been used extensively to characterize Fe_4S_4 clusters, both in complexes and in metalloproteins [1]. It is clear that the precise geometry of an Fe_4S_4 cluster is a function of the grouping bound to the iron (generally a thiolate) though it also varies with the counter cation to some degree [2]. We report here a strong dependence of the Mössbauer quadrupole splitting on the counter cation in a series of salts of $[Fe_4S_4(SBu^t)_4]^{2-}$.

The isomer shift, δ, is a measure of the s-electron density at the iron nuclei, whereas the quadrupole splitting, Δ, is a measure of the asymmetry of the ligand field at the nucleus [3]. Table I shows that all the clusters (as is usual for the $Fe_4S_4^{2+}$ oxidation level) show the presence of a single kind of iron (despite formally containing two iron(II) and two iron(III)) with similar isomer shifts. However, for these salts of $[Fe_4S_4(SBu^t)_4]^{2-}$ the quadrupole splitting covers a surprisingly large range, from 0.78 mm s^{-1} at one extreme to 1.22 mm s^{-1} at the other. There seems a rough correlation with size, the smaller the cation, the smaller the splitting.

The implication of these data is that there must be a mechanism whereby the cation in the crystal disturbs the ligand field around the iron atoms. It is not clear what this mechanism is or how it operates, though a consideration of crystal packing forces would be useful. The reported X-ray crystal structure data for $(Et_4N)_2[Fe_4S_4(SBu^t)_4]$ and $(PhCH_2NMe_3)_2[Fe_4S_4(SBu^t)_4]$ [4] show (i) that the two Fe_4S_4 cores are distorted from T_d symmetry to different extents and (ii) that in the latter there is a sulphido-sulphur...methyl contact of only 3.55 Å, considerably less that the van der Waals' separation, and absent in the former. We therefore suggest that this contact plays a role in the core distortion, and causes the smaller quadrupole splitting of the latter as compared to the former, and are currently determining the structures of $(Me_4N)_2[Fe_4S_4(SBu^t)_4]$ and $(Bu_4N)_2[Fe_4S_4(SBu^t)_4]$ to test the hypothesis.

It has been observed [5] that whereas the isomer shift of ferredoxin and high-potential iron–sulphur proteins in the $Fe_4S_4^{2+}$ oxidation level is relatively invariant at about 0.42 mm s^{-1} (*cf.* the isomer shifts in Table I), the quadrupole splitting is sensitive to the whole protein, and values ranging from *ca.* 0.9 to *ca.* 1.2 mm s^{-1} have been reported. However, the source of this sensitivity has not been identified, although hydrogen-bonding interactions between protein amide groups and sulphido-sulphur, and between amide groups and cysteinyl sulphur may be significant. Our observations reported here suggest that hydrogen bonding may not be limited to N–H...S interactions, and provide a basis for establishing the mechanism of the interdependence of the protein structure and the quadrupole splitting.

TABLE I. Mössbauer Parameters for $Q_2[Fe_4S_4(SBu^t)_4]$ at 77 K

Q	δ (mm s^{-1})	Δ (mm s^{-1})	$\Gamma_{1/2}$[a] (mm s^{-1})
Me_4N	0.45(1)	0.78(1)	0.31(1)
Et_4N	0.43(1)	1.14(1)	0.23(1)
Bu_4N	0.44(1)	1.22(1)	0.21(1)
PPh_4	0.44(1)	0.97(1)	0.23(1)
$BzNMe_3$	0.43(1)	1.10(1)	0.19(1)
$BzNEt_3$	0.43(1)	1.16(1)	0.21(1)
$BzNBu_3$	0.43(1)	1.18(1)	0.24(1)

[a]Width of band at half height.

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