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Low-Coordinate Homoleptic Iron(II) Thiolates Revisited

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Introduction

Six of the seven iron atoms in the iron−molybdenum cofactor of molybdenum nitrogenase from *Azotobacter vinelandii* have recently been described[2] as 3-coordinate with a distorted trigonal geometry. Iron complexes with low coordination number are relatively rare. Power and co-workers have reported the synthesis, structural characterization and Mössbauer spectra of homoleptic 2- and 3-coordinate iron(II) thiolates.[3−5] The Mössbauer spectral parameters were related to the structural data and it was tentatively concluded that trigonal planar and tetrahedral iron thiolate can be distinguished by a difference in the quadrupole splitting. Here we offer a reinterpretation of the Mössbauer and crystallographic data, together with some new Mössbauer results, and show that the coordination number and geometry about iron is best reassigned in some cases. Further, Mössbauer quadrupole splitting can indeed distinguish the coordination geometry about iron in low-coordinate iron complexes, but not in the way previously proposed.

Experimental Section

All manipulations were performed under dinitrogen. The iron(II) thiolate complexes $[\{Fe(SR)_2\}_2]$ (R = $C_6H_2{}^tBu_3$-2,4,6 (**1**) or C_6H_2Ph-2,4,6 (**2**))[3,4] and $[Fe_3(SC_6H_2{}^iPr_3\text{-}2,4,6)_4\{N(SiMe_3)_2\}_2]$[5] (**3**) were prepared as described. $[\{Fe(SR)_2\}_2]$ complexes (R = $C_6H_2Me_3$-2,4,6 or C_6F_5) were prepared by methods analagous to those published.[3,4] Three-coordinate iron(II) amides $[\{Fe\{N(SiMe_3)_2\}_2\}_2]$[6] and $[Fe\{N(SiMe_3)_2\}_2(thf)]$[7] were prepared by literature methods.

Mössbauer spectra were recorded on an ES-Technology MS105 spectrometer at 77 K, using a 925 MBq ^{57}Co source in a rhodium matrix, and were referenced against iron foil (25 μm) at 298 K. All measurements were at zero field on samples in the solid state.

Crystallographic data were retrieved from files of the Cambridge Crystallographic Data Centre via the CSSR routines of the Chemical Database Service at the Daresbury Laboratory.

Results and Discussion

Mössbauer parameters for a series of homoleptic iron(II) thiolate dimers are collected in Table 1. Values obtained previously[5] compare well with those reported here for related complexes. The isomer shift (i.s.) values, in the range 0.77−0.82 mm s^{-1}, are characteristic of high-spin iron(II) and are independent of substituents on the arene ring of the thiolates. Quadrupole splitting values in the range 2.28−2.80 mm s^{-1} are observed. Similar parameters (i.s. = 0.74, q.s. = 2.91 mm s^{-1} at 100 K) have been reported for the monomeric iron(II) dithiolate complex $[Fe(SC_6H_3(mes)_2\text{-}2,6)_2]$, **4** (mes = mesityl).[5] The crystal structures of complexes **1**,[3] **2**,[4] and **4**[8] have been published, and it has been concluded that the iron atoms in **1** and **2** are 3-coordinate and the iron atom in **4** is 2-coordinate. Although it was recognized[5] that in **1** there is an Fe···H distance of ca. 1.8 Å and that in **2** and **4** there are relatively short Fe···C separations of ca. 2.5 Å from adjacent phenyl rings, no Fe···H or Fe···C interactions were "construed as coordinative". The Mössbauer parameters show the electronic environment about the iron atoms in **1**, **2**, and **4** are virtually identical, and we infer from this that the bonding that the iron atoms "see" must also be very similar. Thus, in each of these complexes, and, because of the agostic interactions between iron and protons or iron and the carbons/π-cloud of phenyl rings, which we believe are significant, we consider that the geometry about iron is best described as distorted tetrahedral 4-coordinate.

The complex $[Fe(SC_6H_2{}^tBu_3\text{-}2,4,6)_3]^-$ is 3-coordinate,[5] the shortest Fe···H distance is ca. 2.4 Å and the shortest Fe···C distance ca. 3.3 Å. The Mössbauer parameters for this complex, Table 2, are similar to those of $[Fe(SC_6H_3(mes)_2\text{-}2,6)\{N(SiMe_3)_2\}]$, **5**, previously described[5,8] as containing 2-coordinate iron. Again, reexamination of the crystallographic data for this molecule shows that the geometry about the iron of **5** can be redefined. The distance from the iron atom to the center of one of the mesityl rings of the thiolate is 2.17 Å, suggesting an interaction with the π-cloud, even though the distances from the iron atom to individual carbon atoms in the ring are 2.46−2.69 Å. Molecule **5** is, therefore, best described as trigonal planar 3-coordinate. This interpretation accounts for the unexplained[5] large difference in q.s. between complexes **4** and **5** previously both described as 2-coordinate. The Mössbauer parameters for two other high-spin iron(II) trigonal planar complexes[7] have been measured for comparison, Table 2. In these bis(hexamethyl)disilylamide−iron(II) complexes, the i.s. values are similar to those found for trigonal homoleptic iron(II) thiolates. The larger q.s. of $[Fe\{N(SiMe_3)_2\}_2(thf)]$ may be due to a combination of the presence of oxygen in the coordination environment of, and to greater asymmetry about, the iron atom. The lower i.s. values, 0.53−0.66 mm s^{-1}, for 3-coordinate complexes compared to those of complexes with higher coordination number arise from a covalency effect and are consistent with the trend for high-spin iron(II) of increasing i.s. with increase in coordination number.

Power and co-workers[5] could not fit the Mössbauer spectrum, at 100 K, of the trinuclear mixed ligand complex $[Fe_3(SC_6H_2\text{-}{}^iPr_3\text{-}2,4,6)_4\{N(SiMe_3)_2\}_2]$ (**3**) to give parameters consistent with their correlation of q.s. to iron coordination number. We have recently reported[9] the Mössbauer spectrum, at 77 K, of complex **3** and shown that the central iron, which is 4-coordinate with very distorted tetrahedral geometry, has an i.s. of 0.78 mm s^{-1} and an extremely large q.s. of 4.55 mm s^{-1}. The terminal iron atoms, described previously[5,9] as 3-coordinate, exhibit a broad doublet ($\Gamma_{1/2}$ = 0.74 mm s^{-1}) with i.s. of 0.84 and q.s. of 3.60 mm s^{-1}. Both the i.s. and q.s. are larger than expected (see above) for 3-coordinate iron atoms. Examination of the crystallographic data[5] shows that there are Fe···H interactions

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Table 1. Mössbauer Parameters, Zero Field, for Homoleptic Iron(II)−Thiolate Dimers

complex	temp (K)	i.s (mm s^{-1})	q.s (mm s^{-1})[b]	hwhm[a]	ref
$[\{Fe(SC_6H_2{}^tBu_3\text{-}2,4,6)_2\}_2]$ (**1**)	77	0.77(1)	2.47(1)	0.21(1)	this work
	100	0.77	2.49	0.20	5
$[\{Fe(SC_6H_2Ph_3\text{-}2,4,6)_2\}_2]$ (**2**)	4.2	0.77	2.28	0.27	5
$[\{Fe(SC_6H_2Me_3\text{-}2,4,6)_2\}_2]$	77	0.82(1)	2.80(1)	0.20(1)	this work
$[\{Fe(SC_6F_5)_2\}_2]$	77	0.80(1)	2.65(1)	0.30(1)	this work

[a] hwhm = half-width at half maxima (mm s^{-1}). [b] Value in parentheses is error in last decimal place.

Table 2. Mössbauer Parameters, Zero Field, for 3-Coordinate Iron(II) Complexes

complex	temp (K)	i.s (mm s^{-1})	q.s (mm s^{-1})[b]	hwhm[a]	ref
$[Fe(SC_6H_2{}^tBu_3\text{-}2,4,6)_3]^-$	100	0.53	0.81	0.21	5
	4.2	0.57	0.81	0.11	5
$[Fe(SC_6H_3(mes)_2\text{-}2,6)\{N(SiMe_3)_2\}]$ (**5**)	4.2	0.66	0.79	0.18	5
$[Fe\{N(SiMe_3)_2\}_2(thf)]$	77	0.57(1)	1.97(1)	0.19(1)	this work
$[\{Fe\{N(SiMe_3)_2\}_2\}_2]$	77	0.58(1)	1.02(1)	0.22(1)	this work

[a] hwhm = half-width at half maxima (mm s^{-1}). [b] Value in parentheses is error in last decimal place.

of 2.37 and 2.42 Å for one of the terminal iron atoms and 2.58 and 2.69 Å for the other. These "long-range" interactions may influence the electric field gradient experienced by the iron atoms, and by Mössbauer criteria the terminal iron atoms can be considered as 5-coordinate. The large line width may arise from the overlap of quadrupole split doublets from each of the terminal iron atoms together with magnetic relaxation effects.

To summarize, consideration of both crystallographic and Mössbauer data has led to the redefinition of the coordination number of iron in several low-coordinate high-spin iron(II) thiolates. The iron atoms of the dimeric homoleptic iron(II) thiolate complexes $[Fe_2(SC_6H_2{}^tBu_3\text{-}2,4,6)_4]$ (**1**) and $[Fe_2(SC_6H_2Ph_3\text{-}2,4,6)_4]$ (**2**) are not 3- but 4-coordinate. The complexes $[Fe(SC_6H_3(mes)_2\text{-}2,6)\{N(SiMe_3)_2\}]$ (**5**) and $[Fe\{SC_6H_3(mes)_2\text{-}2,6\}_2]$ (**4**), formerly both described as containing 2-coordinate iron, have 3- and 4-coordinate iron, respectively, and the terminal iron atoms of $[Fe_3(SC_6H_2{}^iPr_3\text{-}2,4,6)_4\{N(SiMe_3)_2\}_2]$ (**3**) are, by Mössbauer criteria, 5- and not 3-coordinate. Trigonal planar high-spin iron(II) thiolates have characteristic Mössbauer parameters, i.s. ca. 0.6 mm s^{-1}, and q.s. ca. 0.8 mm s^{-1} and can, therefore, be readily distinguished from tetrahedral and other geometries about iron. From the discussion above it can also be concluded that there are no unambiguous examples of 2-coordinate iron(II) thiolates.

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Additions and Corrections

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Ewan J. M. Hamilton, Glenn T. Jordan IV, Edward A. Meyers, and Sheldon G. Shore*: One-Step Preparation of Dimethyl Sulfide Substituted Icosahedral Boranes: The Crystal and Molecular Structures of $1,7\text{-}(SMe_2)_2B_{12}H_{10}$, $1,12\text{-}(SMe_2)_2B_{12}H_{10}$, and $[SMe_3][B_{12}H_{11}(SMe_2)]\cdot MeCN$.

Page 5335. In column 1, the following addendum belongs at the end of the first paragraph:

However, more recently, Jasper, Jones, Mattern, Huffman, and Todd[13] reported that from the reaction of Me_2SPdCl_2 with $Li_2[B_{12}H_{12}]$ they obtained a mixture of products from which they separated the $1,7\text{-}(Me_2S)_2B_{12}H_{10}$ and $1,12\text{-}(Me_2S)_2B_{12}H_{10}$ isomers. Identification was based upon comparison of ^1H NMR and IR spectra with those reported by Wright and Kaczmarczyk[4] for a mixture of isomers.

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Zuowei Xie,* Ka-yue Chiu, Bomu Wu, and Thomas C. W. Mak: Autoionization of SmI_3 in Tetrahydrofuran. X-ray Crystal Structure of the Ionic Complex $[SmI_2(THF)_5][SmI_4(THF)_2]$.

Page 5957. In paragraph 1, the word "tetrahydrofuran" was inadvertently omitted from the sentence beginning on line 12. The correct sentence should read as follows: To date, no crystal structure of any LnI_3 tetrahydrofuran complex has, to our knowledge, been reported. In the reference list, refs 19 and 20 should be interchanged.

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