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Does the ^{57}Fe Mössbauer isomer shift depend on the oxidation state of iron?

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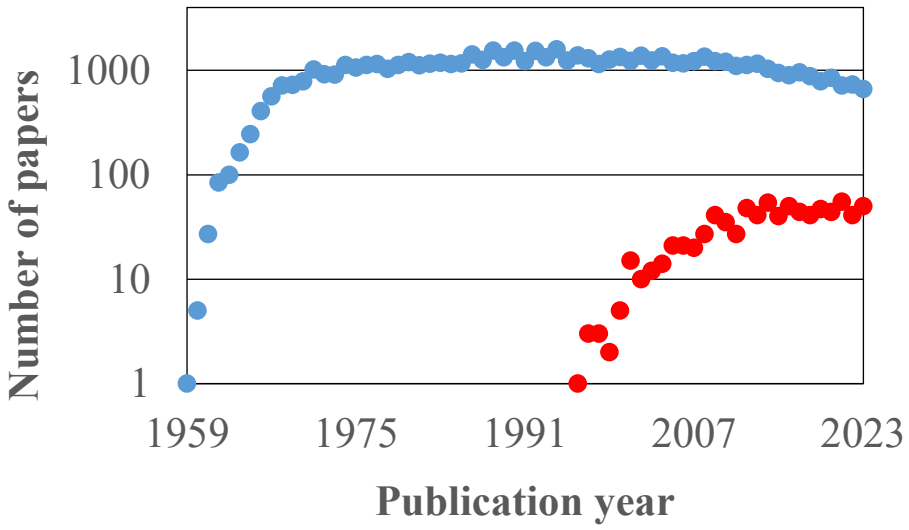

Figure S1 Publication dynamics of journal papers containing the words 'Mössbauer' (blue dots) or 'Mössbauer + DFT' (red dots) in their abstracts or keywords, based on data from CAS SciFinder (https://scifinder-n.cas.org/).

Table S1 Room-temperature isomer shifts for selected iron oxo compounds.[a]

Formula	ICSD[b] deposition number	IS[c]/mm s^{-1}
$K_3Na(FeO_4)_2$	159909	−0.89
K_2FeO_4	32756	−0.90
Cs_2FeO_4	33861	−0.87
K_3FeO_4	65977	−0.56
Na_4FeO_4	59585	−0.22
Na_5FeO_4	2485	0.12
Cs_9FeO_4	174308	0.10
$LiLa_2FeO_6$	252554	−0.41
Sr_2FeO_4	69849	−0.01
$SrFeO_3$	91062	0.05
α-$NaFeO_2$	420380	0.33
α-Fe_2O_3 (hematite)	245851	0.37
$Ca_3Fe_2(SiO_4)_3$ (andradite)	203209	0.41
β-$NaFeO_2$	14779	0.18
Sr_2FeO_3	251020	0.42
$Sr_3Fe_2O_5$	261512	0.46
$SrFeO_2$	418603	0.50
$BaFeSi_4O_{10}$ (gillespite)	31202	0.77
$FeCr_2O_4$ (chromite)	250575	0.94
FeO (wustite)	82233	1.08
$Fe_3Al_2(SiO_4)_3$ (almandine)	80671	1.28

[a] The table is adapted from reference S1. [b] ICSD is the Inorganic Crystal Structure Database.[S2] [c] Isomer shifts are presented relative to α-iron, their uncertainties do not exceed 0.02 mm s^{-1}.

Table S2 Isomer shifts at liquid nitrogen temperature for selected organoiron compounds.[a]

Complex	Formula	CCDC[b] deposition number	CCDC identifier	IS[c]/mm s^{-1}
5	[(TIMMN^{Mes*})Fe(=N*)(NCMe)]$(PF_6)_2(MF_6)$, M=Mo, Re	2258914	XOJPAR	−0.16
1	[(TIMMN^{Mes})Fe(N)](PF_6)	2020254	AKEJEI	−0.35
2	[(TIMMN^{Mes})Fe(N)]$(PF_6)_2$	2020255	AKEJIM	−0.47
6	[(TIMMN^{Mes*})Fe(NH*)(F)]$(PF_6)_3$	2297600	XOJPEV	*no data*
3	[(TIMMN^{Mes})Fe(N)(F)]$(PF_6)_2$	2258913	XOJNUJ	−0.60
4	[(TIMMN^{Mes})Fe(N)(F)]$(PF_6)_2(PF_6/MF_6)$, M=Mo, Re	*no structural data*		−0.72
	[(ImMes-)$_3$-BPh]Fe(N-adamantyl)	616728	MOBNEX	−0.11
	{[(ImMes-)$_3$-BPh]Fe(N-adamantyl)}[BPh_4]	631683	MOBNUN	−0.17
	[(Im^{t}Bu-)$_3$-BPh]Fe(N)	1549741	HAQLAP	−0.32
	[(ImMes-)$_3$-BPh]Fe(N)	1549742	HAQLET	−0.35
	[{[ImMes(C_2H_4-)]$_3$-N}Fe(N)][BPh_4]	676550	TIYJOB	−0.27
	{[(Im^{t}Bu-)$_3$-BPh]Fe(N)}[$BArF_{24}$]	786059	APUQIM	−0.45
	[(ImMes-)$_2$-BH_2]Fe(N-Mes)$_2$	1990357	ZACWUZ	−0.25
	{[(ImMes-)$_2$-BH_2]Fe(N-Mes)$_2$}[BPh_4]	1990356	ZACXAG	−0.48
	{[(ImMe-)$_3$-BPh]$_2$Fe}[PF]$_6$	1842079	BIRWAD	***−0.05***[d]
	{[(ImMe-)$_3$-BPh]$_2$Fe}[PF_6]$_2$	1961137	ERUXIB	−0.23

[a] The table is adapted from references S3 and S4. [b] CCDC is the database of the Cambridge Crystallographic Data Centre.[S5] [c] The isomer shifts are presented relative to α-iron at room temperature, their uncertainties do not exceed 0.02 mm s^{-1}. [d] The isomer shift of BIRWAD was calculated by adding 0.10 mm s^{-1} to the room-temperature value.

Table S3 Structural information for the previously known compounds.[a]

Complex	Formula	Interatomic distances[b]/pm							
		$aID_{Fe–X}$	Fe–C	Fe–C	Fe–C	Fe–N	Fe–N[c]	Fe–NC	Fe–F
5	$[(TIMMN^{Mes*})Fe(=N*)(NCMe)](PF_6)_2(MF_6)$, M=Mo, Re	190	186	198	198	168	*217*	203	
1	$[(TIMMN^{Mes})Fe(N)](PF_6)$	185	194	196	198	153	*233*		
2	$[(TIMMN^{Mes})Fe(N)](PF_6)_2$	182	192	193	193	150	*243*		
6	$[(TIMMN^{Mes*})Fe(NH*)(F)](PF_6)_3$	192	179	197	197	175	*210*		206
3	$[(TIMMN^{Mes})Fe(N)(F)](PF_6)_2$	186	197	198	199	152	*235*		187
4	$[(TIMMN^{Mes})Fe(N)(F)](PF_6)_2(PF_6/MF_6)$, M=Mo, Re	*no data*							

[a] The table is adapted from reference S3. [b] The interatomic distances are rounded to picometers. [c] The Fe–N distances marked in *italics* were not taken for the calculations of the $aID_{Fe–X}$.

Table S4 Mössbauer isomer shifts and structural information for the hemoglobin and related compounds.[a]

Complex	RCSB PDB[b] entry ID or CCDC identifier	$IS_{\alpha\text{-}Fe}$[d]/ mm s^{-1}	X	Interatomic distances[c]/pm						
				$aID_{Fe–X}$	Fe–X	Non-hem Fe–N	Fe–N in hem			
DeoxyHbA-α	2DN2	0.89		210		221	202	208	210	210
				213		220	208	211	212	212
DeoxyHbA-b				208		216	204	206	207	208
				212		219	208	209	210	212
OxyHbA-α L	2DN1	0.23	O_2	199	182	207	200	201	202	202
OxyHbA-b L			O_2	199	178	206	198	199	200	211
CO-HbA-α L	2DN3	0.23	CO	198	171	212	196	203	203	203
CO-HbA-b L			CO	200	174	211	202	203	203	209
porphyrinato-iron(II)	DEDWUE	***0.62***		200			199	199	201	201
imidazol-porphyrinato-iron(II)	WENPAJ	0.89		210		216	207	208	209	209
pyrazol-porphyrinato-iron(II)	AMAJII	0.89		209		215	206	207	207	209
bis-imidazol-porphyrinato-iron(II)	EWURUL	0.38	N	199	199	199	198	198	199	200
bis-imidazol-porphyrinato-iron(III)	LEVHOK	0.35	N	198	200	201	197	197	197	198
imidazol-dioxygen-porphyrinato-iron	DOGWED	0.28	O	198	186	206	199	199	199	199

[a] References S6–S14. [b] RCSB PDB is RCSB Protein Data Bank,[S6] https://www.rcsb.org/. [c] The interatomic distances are rounded to picometers. [d] The isomer shifts correspond to temperatures close to the temperature of liquid nitrogen, with the exception of DEDWUE value (bold italic), which refers to the liquid-helium temperature. The uncertainties do not exceed 0.03 mm s^{-1}.

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