Partial Mössbauer Centre Shifts in Low-spin Iron(II) Compounds: a Correlation with the Spectrochemical Series

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MÖSSBAUER studies [1,2] on iron compounds have indicated that the Mössbauer centre shifts (C.S.)† are an approximate additive property of the number and type of ligands bonded to the iron atom, and that it is therefore possible to assign partial centre shifts (P.C.S.) to individual ligands. For low-spin Fe[II] compounds Erickson has, in addition, tentatively suggested a relationship between centre shifts and the spectrochemical series.[1] Neither this correlation nor the P.C.S. concept has, however, been well established for low-spin Fe[II] compounds.

We now present room temperature centre shifts for eighteen Fe[II] low-spin compounds of the type FeX_2Y_4 (X = H, Cl, Br, I, $SnCl_3$, or SiH_3; Y = depe/2, depb/2, ArNC, or CO) together with selected literature data[1,3,4] (Table 1) which show that P.C.S. values may indeed be derived, and that these correlate well with the spectrochemical series.

We calculate our P.C.S. values relative to stainless steel, and assume that the P.C.S. value for ArNC is equal to that for other isocyanides (*ca.* 0·00 mm./sec.). We also assume

† C.S. = I.S. + S.O.D. + Z.P.M., where I.S. = isomer shift; S.O.D. = second-order Doppler shift, and Z.P.M. = zero-point motion shift (Y. Hazony, *J. Chem. Phys.*, 1966, **45**, 2664.)

TABLE 1

Compound	C.S.*	Ref.	Compound	C.S.* Found	C.S.* Calc.	Ref.
(1) trans-FeCl₂(ArNC)₄†	0·20	a	(22) cis-FeCl₂(ArNC)₄	0·12	0·20	a
(2) trans-Fe(SnCl₃)₂(ArNC)₄	0·08	a	(23) cis-Fe(SnCl₃)₂(ArNC)₄ ..	0·11	0·08	a
(3) trans-FeCl₂ depe₂†	0·43	a		(±0·03)		
(4) trans-FeBr₂ depe₂	0·50	a	(24) cis-FeCl(SnCl₃)(ArNC)₄ ..	0·09	0·14	a
(5) trans-FeI₂ depe₂	0·49	a	(25) [FeCl(ArNC)₅]ClO₄	0·06	0·10	a
(6) trans-FeBr₂ depb₂†	0·45	a		(±0·02)		
(7) trans-FeH₂ depb₂	0·05	a	(26) [Fe(SnCl₃)(ArNC)₅]ClO₄ ..	0·02	0·04	a
(8) cis-FeH₂(CO)₄‡	−0·15	a	(27) trans-FeHCl depe₂	0·23	0·26	a
(9) cis-Fe(SiH₃)₂(CO)₄‡	−0·10	b	(28) trans-FeHI depe₂	0·23	0·29	a
(10) [Fe(MeNC)₆](HSO₄)₂	−0·02	c	(29) trans-FeCl(SnCl₃) depe₂ ..	0·39	0·38	a
(11) [Fe(EtNC)₆](ClO₄)₂	0·00	c	(30) trans-FeCl₂ depb₂	0·43	0·40	a
(12) K₄[Fe(CN)₆]	0·05	d	(31) K₃[Fe(CN)₅CO]	−0·01	0·05	d
(13) Na₂[Fe(CN)₅NO],2H₂O ..	−0·16	d	(32) trans-Fe(CN)₂(MeNC)₄ ..	0·00	0·02	c
(14) Na₅[Fe(CN)₅SO₃]	0·06	e	(33) [Fe(CN)(EtNC)₅]ClO₄ ..	0·04	0·01	c
(15) Na₄[Fe(CN)₅NO₂]	0·10	e	(34) K₂[Fe dipy (CN)₄] ..	0·16	0·16	d
(16) Na₃[Fe(CN)₅NH₃],H₂O ..	0·10	e	(35) K₂[Fe phen (CN)₄] ..	0·17	0·18	d
(17) Fe niox₂ py₂†	0·30	f	(36) cis-Fe dipy ₂(CN)₂ ..	0·27	0·26	d
(18) K₂[Fe niox₂(CN)₂]‡	0·18	f	(37) cis-Fe phen ₂(CN)₂ ..	0·26	0·30	d
(19) PcFe py₂†	0·35	f	(38) "trans"-Fe phen ₂(CN)₂ ..	0·32	0·30	d
(20) [Fe dipy₃](ClO₄)₂†	0·36	d	(39) Fe niox ₂(NH₃)₂	0·30	0·26	f
(21) [Fe phen₃](ClO₄)₂†	0·41	d	(40) K₂[pc Fe(CN)₂]‡	0·21	0·22	f

* Error in our results = 0·01 mm./sec., except where quoted. Values quoted relative to stainless steel.

† ArNC = p-methoxyphenyl isocyanide; depe = bis(diethylphosphino)ethane; depb = o-phenylenebis(diethylphosphine); niox = cyclohexane-1,2-dione dioxime; py = pyridine; pc = phthalocyanine; dipy = 2,2'-bipyridyl; phen = o-phenanthroline.

‡ Value quoted estimated from spectra at 80° K.

a. This work.

b. B. J. Aylett, personal communication (B. J. Aylett, P. R. Berrett, J. M. Campbell, and B. W. Fitzsimmons, unpublished work).

c. Ref. 5.   d. Ref. 1a.   e. Ref. 4.   f. Ref. 7a.

that any changes in C.S. are due to changes in isomer shift. The P.C.S. values for the ligands listed in Table 2 have been calculated using the C.S. of compounds 1—21. The other compounds (22—40) act as cross-checks. With the

TABLE 2

Ligand	P.C.S.*	Ligand	P.C.S.*
NO	−0·20	NO₂	0·05
H	−0·08	NH₃	0·05
SiH₃	−0·05	Pc/4	0·05
ArNC	0·00	depb/2	0·05
MeNC	0·00	depe/2	0·06
EtNC	0·00	dipy/2	0·06
CO	0·00	phen/2	0·07
CN	0·01	py	0·07
SO₃	0·01	Cl	0·10
SnCl₃	0·04	Br	0·13
niox/2	0·04	I	0·13

* Estimated error = 0·01 mm./sec., except for the Fe(CN)₅X series, where since only one X is present the estimated error is ≤ 0·02 mm./sec.

exception of compounds 22, 28, 31, the C.S. values predicted for these compounds from the P.C.S. values are in good agreement with the observed values. The P.C.S. values

are thus essentially independent of the nature of the other ligands present.‡

The order of P.C.S. values is very similar to the spectrochemical ranking of ligands.[5] This is not surprising because just as the spectrochemical Δ should increase with an increase in σ-bonding (L → M) and π back-bonding (M → L),[6] so the P.C.S. values should decrease.§ Thus, the ligand having the lowest (most negative) P.C.S. (NO⁺) gives the largest value of Δ. Erickson[1] and Fluck et at.[3] considered that changes in π-bonding were responsible for the change in centre shifts in iron(II) cyanide derivatives, but the P.C.S. value for H⁻, a strong σ-donor, indicates that σ-donation can also be very important.

Since there is an inverse relationship between the C.S. and Δ, we expect to find a limiting value of the C.S., above which there will be a transition from a low-spin to a high-spin complex. In a recent study of high-spin–low-spin equilibria,[7] with Fe^II complexes containing the hydrotris-(pyrazol-1-yl)borate ligand, the H,H-substituted ligand gave a low-spin complex with a C.S. of 0·51 mm./sec., while the very similar Me,Me-derivative was high spin. We suggest then that the room temperature upper limit for Fe^II low-spin compounds is ca. 0·5 mm./sec. All octahedral low-spin Fe^II complexes for which C.S. data exist have a C.S. lower than 0·52 mm./sec.

It should also be possible from P.C.S. and quadrupole

‡ As Erickson (ref. 1) has pointed out, the concept of partial shifts will not be completely independent of geometry.

§ With strongly σ-bonding ligands such as H⁻, the correlation may be fortuitous, since the P.C.S. values depend mainly on the interaction of the ligand σ-orbitals with the 4s-orbital of Fe, whereas Δ depends on the interaction of ligand σ-orbitals with Fe e_g orbitals.

splitting data to obtain estimates of the electron-withdrawing and -donating properties of individual ligands. We are currently extending our measurements to determine how well the estimates agree with previous ones based on i.r.,[8] u.v.[9] and n.m.r.[10] data.

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