Correlation between Core-electron Binding Energies and Mössbauer Chemical Isomer Shifts for Inorganic Complexes Containing Iron(II) Low Spin

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Summary For five Fe^{II} low-spin complexes, there is a linear correlation between the ^{57}Fe isomer shifts and the Fe2*p* and Fe3*p* binding energies; the trend in binding energies is related to the π-acceptor properties of the ligands.

The object of this study was to examine the correlation between the shifts in Fe 2*p* and 3*p* binding energies as determined by *X*-ray induced photoelectron spectroscopy, and the corresponding Mössbauer isomer shifts for a series of closely related iron compounds. In a recent study[1] of Sn^{IV} octahedral complexes, the binding energy of the Sn 4*d* electrons were found to change smoothly with the Mössbauer shifts: as expected,[2] the Sn 4*d* binding energy *increased* with increasing electronegativity of the ligands; and, as is common[3] for most Sn compounds, values of isomer shifts (and $[\psi(O)_S]^2$), *decreased* as the electronegativity of the ligands *increased*. For transition-metal complexes, however, the trend in binding energies is more difficult to predict since the metal ligand bonding involves strong π-acceptance as well as σ-donation. For example, for Fe^{II} low spin (t_{2g}^6), the bonding in an octahedral complex may be described by both ligand σ-donation to the Fe d^2sp^3 hybrid and π-acceptance from the t_{2g} *d* orbitals. Considering just intramolecular bonding, as σ-donation *increases*, the binding energy should *decrease*; in contrast, as π-acceptance *increases*, the binding energy should *increase*. Since the isomer shifts decrease as both σ and π effects increase, the slope of a binding energy *versus* isomer shift plot will be negative or positive depending upon whether the binding energies are more sensitive to π-acceptance by the ligand or σ-donation to the metal respectively.

Table. *Absolute binding energies (eV) of certain core-levels for a series of low-spin* Fe^{II} *complexes.*[a]

	Fe $2p_{3/2}$	Fe 3*s*	Fe 3*p*	C 1*s*[b]
$[Fe^{II}(phen)_3][ClO_4]_2$[c]	706·6 ± 0·3	91·2 ± 0·8	54·0 ± 0·5	284·2 ± 0·2
trans-$Fe(isocy)_4Cl_2$[d]	707·3 ± 0·5	—	—	284·2 ± 0·2
trans-$Fe(isocy)_4(SnCl_3)_2$	707·7 ± 0·3	—	54·7 ± 0·5	284·2 ± 0·2
$[Fe(SnCl_3)(isocy)_5][ClO_4]$	708·0 ± 0·4	—	55·2 ± 0·6	284·1 ± 0·2
$Na_2Fe(CN)_5NO{\cdot}2H_2O$	709·1 ± 0·5	—	55·9 ± 0·6	283·7 ± 0·2

[a] The Fe 3*s* peaks were too weak to be satisfactorily measured in most cases. [b] Rather broad peaks occur in most of the compounds. [c] (phen) = 1,10-phenanthroline. [d] (isocy) = *p*-methoxy phenylisocyanide.

The absolute binding energies were determined by means of the gold decoration technique described elsewhere,[5,6] the Au $4f_{7/2}$ level being taken as 84·0 ± 0·3 eV. *X*-ray spectra were recorded on an A.E.I. ES100 employing Al-K_α radiation and isomer shifts were determined as in ref. 4. These compounds covered the entire large range of Fe^{II} low-spin shifts.

The Figure shows that there is a smooth correlation between the Mössbauer isomer shifts and binding energies, there being two interesting observations which arise from these correlations. Firstly, the slope of the line is negative as for the Sn compounds.[1] However, because $\delta R/R$ is positive for Sn but negative for Fe, the *s* electron density at the Fe nucleus *increases* as the binding energy *increases*, in opposition to the trend for Sn. Secondly, the sensitivity of the 2*p* and 3*p* binding energies to ligand variation are similar.

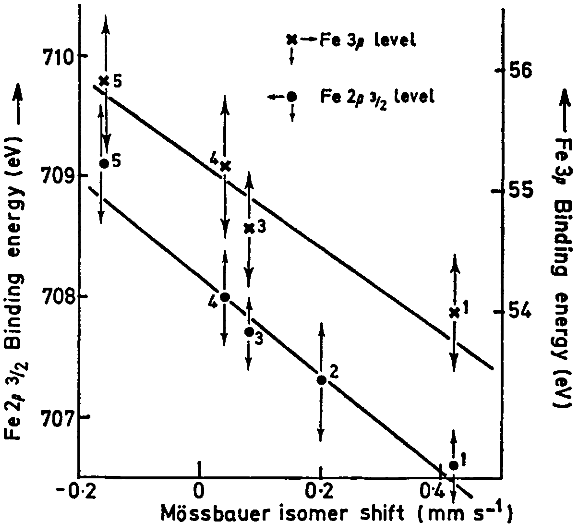

FIGURE. *Plot of Mössbauer isomer shift* versus *absolute binding energy for* Fe $2p_{3/2}$ *and* Fe 3p *levels.* (*The numbers refer to the compounds listed in the Table.*)

Trends in isomer shifts have recently been interpreted successfully[4] considering only intra-molecular bonding. Since the Madelung potential and so-called solid-state effects[7] are likely to be negligible for these molecular compounds, it should also be legitimate to interpret the binding energies by considering only intramolecular bonding. As discussed in the first paragraph of this communication, the negative slope of the line in the Figure strongly suggests that the binding energies are more sensitive to changes in π-acceptance than σ-donation, and that π-acceptance from the Fe atom increases from $Fe(phen)_3(ClO_4)_2$ to $Na_2Fe(CN)_5NO\cdot 2H_2O$. A previous study of Pd complexes[8] also indicates that π-acceptor ligands such as CN^- increase the binding energy of the Pd core levels.

Although it is perhaps surprising that the 2*p* and 3*p* binding energies have broadly similar sensitivities, Clark[9] has recently calculated for the [Cl–H–Cl] ion that the Cl 1*s*, 2*s*, and 2*p* binding energies all have essentially identical sensitivities as the position of the H atom is varied between the Cl atoms.

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[1] M. Barber, P. Swift, D. Cunningham, and M. J. Frazer, *Chem. Comm.*, 1970, 1338.
[2] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, in "E.S.C.A. Applied to Free Molecules," North Holland, 1969.
[3] R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, in the press.
[4] G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.
[5] J. M. Thomas, E. L. Evans, M. Barber, and P. Swift, *Trans. Faraday Soc.*, 1971, **67**, 1875.
[6] J. M. Thomas, I. Adams, and M. Barber, *Solid State Comm.*, 1971, **9**, 1571.
[7] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindberg, and B. Lindgren, E.S.C.A. (Almquist and Wiksells, Boktryckeri AB, Uppsala, 1967).
[8] G. Kumar, J. R. Blackburn, R. G. Aldridge, W. E. Moddeman, and M. M. Jones, *Inorg. Chem.*, 1972, **11**, 296.
[9] D. T. Clark, personal communication.