High-spin Iron(II) Chelate Complexes with β-Diketonate and Schiff Base Ligands: Mössbauer and Electronic Spectra

By **Joop L. K. F. de Vries, Jan M. Trooster,** and **Engbert de Boer,*** Department of Physical Chemistry, University of Nijmegen, Nijmegen, The Netherlands

A number of high-spin iron(II) chelate complexes with some bidentate monoanionic ligands (β-diketonates, salicylaldehydate, and *N*-alkylsalicylideneiminates) and the quadridentate dianion *NN'*-ethylenebis(salicylideneiminate), and its analogues, has been studied by means of Mössbauer and electronic spectroscopy. In all the complexes the iron atom is probably six-co-ordinate because of intermolecular interactions, even in complexes of the quadridentate ligands. The isomer shifts mainly depend on the nature of the ligand atoms bound directly to the iron. For a series of closely related complexes, a linear relation has been observed between isomer shifts and quadrupole splittings. From an analysis of the temperature dependence of the quadrupole splitting, it may be inferred that the complexes studied undergo large axial distortion. This conclusion also rationalizes the relatively narrow range (2·0—2·9 mm s^{-1}) of quadrupole splittings observed.

IN this paper high-spin iron(II) chelate complexes are discussed which contain ligands, (I)—(IV), binding to the iron atom through oxygen atoms or through oxygen and nitrogen atoms. Compared to the vast amount of information available on complexes of these ligands with bivalent Ni, Cu, Zn, and Co,[1] only little is known for those with high-spin iron(II). There are several reasons for this. First, most high-spin iron(II) chelate complexes are very air-sensitive and can only be prepared and handled under anaerobic conditions. In a previous communication [2] we showed that all Mössbauer spectra of iron(II) complexes with Schiff bases [(III) and (IV)] reported so far were actually measured on oxidation products;[3] this conclusion has recently been confirmed by Fitzsimmons *et al.*[4] Secondly, for several chelate complexes a reproducible preparation procedure is hard to find because of the occurrence of polymerization, solvation effects, or binding of neutral unidentate ligands. Thirdly, many experimental techniques, such as magnetic resonance and *X*-ray crystallography, require samples of high purity or single crystals; this makes

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[1] (*a*) A. E. Martell and M. Calvin, 'Chemistry of the Metal Chelate Compounds,' Prentice Hall, New York, 1952; (*b*) R. H. Holm, G. W. Everett, jun., and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83; (*c*) J. P. Fackler, jun., *ibid.*, p. 361; (*d*) 'Spectroscopy and Structure of Metal Chelate Compounds,' eds. K. Nakamoto and P. J. McCarthy, John Wiley, New York, 1968.

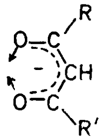
[2] J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Chem. Comm.*, 1970, 604.

[3] (*a*) K. Burger, L. Korecz, J. B. A. Manuaba, and P. Mag, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1673; (*b*) R. A. Stukan, V. I. Goldanskii, E. F. Makarov, and E. G. Ruchadse, *Zhur. strukt. Khim.*, 1967, **8**, 239; (*c*) E. Fluck in 'Chemical Applications of Mössbauer Spectroscopy,' eds. V. I. Goldanskii and R. H. Herber, Academic Press, New York, 1968, p. 268; (*d*) V. I. Goldanskii, *Organometallic Chem. Rev.* (*A*), 1969, **4**, 225; (*e*) L. Korecz and K. Burger, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1673; (*f*) D. S. Kulgawczuk, B. Sawicka, I. Stronski, E. Nowicka, J. Sawicki, and K. Tomala, *Acta Phys. Polon.*, 1970, **A37**, 891.

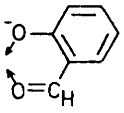
[4] B. W. Fitzsimmons, A. W. Smith, L. F. Larkworthy, and K. A. Rogers, *J.C.S. Dalton*, 1973, 676.

these techniques less suitable for characterization of new iron(II) chelate complexes. As far as the Mössbauer technique is concerned, small amounts of impurities do not interfere.

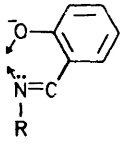
In this work all chelate complexes were prepared and purified in vacuum, and were investigated in the solid state by means of Mössbauer and electronic spectroscopy. The Mössbauer spectra especially give insight into the degree of covalency of the iron–ligand bonds and the type of co-ordination of the iron atom. Small symmetry distortions were observed and the occurrence of structurally different species was clearly reflected in the spectra. In this paper, results will first be discussed for all three types of chelate complexes studied, followed by a consideration of the nature of the chemical bonding in the complexes, and finally some details on the preparation procedures are given.



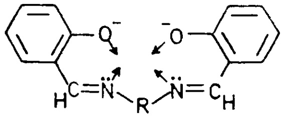
(I) R = R′ = Me (pd)
R = Me, R′ = Ph (pbd)
R = R′ = Ph (dppd)



(II) sala



(III) R = Me (Mesal)
R = Et (Etsal)
R = Pr^n (Pr^{n}sal)
R = Pr^i (Pr^{i}sal)
R = Bu^n (Bu^{n}sal)
R = Bu^i (Bu^{i}sal)
R = Bu^t (Bu^{t}sal)



(IV) R = $(CH_2)_2$ (ensal)
R = $(CH_2)_3$ (pnsal)
R = $(CH_2)_4$ (bnsal)
R = o-C_6H_4 (phnsal)

RESULTS AND DISCUSSION

Chelate Complexes with Two Oxygen Atoms as Binding Sites [*Ligands* (I) *and* (II)].—Mössbauer parameters of these complexes are given in Table 1. In Figure 1 the isomer shifts (i.s.) and quadrupole splittings (q.s.) are correlated. The i.s. values are characteristic for high-spin iron(II). This confirms results from earlier susceptibility measurements.[5] Data for the 1,3-diphenylpropane-1,3-dionate (dppd) complexes are in agreement with the results of Takashima *et al.*[6]

The q.s. of high-spin iron(II) is rather sensitive to the type of co-ordination and symmetry. It is generally accepted that $[Fe(L_2)L_2']$ (L = β-diketonate or salicylaldehydate; L′ = H_2O, NH_3, pyridine, or piperidine) complexes contain six-co-ordinate iron,[5a] similarity of the q.s. of $[Fe(L_2)L'_2]$ and $[FeL_2]$ complexes suggesting six-co-ordination for the latter as well. This points to a

TABLE 1

Mössbauer parameters (mm s^{-1}) of $[Fe(L_2)L'_2]$ and $[FeL_2]$ chelate complexes with oxygen-binding ligands L, measured at 95 K. The isomer shift (i.s.) in this and following Tables is given with respect to the salt $Na_3[Fe(CN)_5(NO)]$. The accuracy of the data is *ca.* 0·01 mm s^{-1}

	Isomer shift (i.s.)	Quadrupole splitting (q.s.)	Colour
$[Fe(pd)_2],1\cdot5H_2O$	1·51	2·64	Brown
$[Fe(pd)_2(NH_3)_2]$	1·46	2·81	Brown
$[Fe(pd)_2(pip)_2]$	1·47	2·73	Brown
$[Fe(pd)_2(py)_2]$	1·41	2·40	Brown
$[Fe(dppd)_2(H_2O)_2]$	1·50	2·53	Violet-blue
$[Fe(dppd)_2(NH_3)_2]$	1·43	2·63	Violet-blue
$[Fe(dppd)_2(pip)_2]$	1·37	2·14	Blue
$[Fe(dppd)_2(py)_2]$	1·39	2·27	Dark green
$[Fe(sala)_2(H_2O)_2]$	1·48	2·50	Violet
$[Fe(sala)_2(py)_2]$	1·42	2·54	Black
$[Fe(pbd)_2(H_2O)_2]$	1·50	2·55	Violet
$[Fe(pbd)_2(NH_3)_2]$	1·45	2·87	Blue
$[Fe(pbd)_2(pip)_2]$	1·43	2·51	Dark blue
$[Fe(pbd)_2(py)_2]$	1·43	2·48	Brownish red
$\{Fe(pd)_2\}_n$	1·59 1·49	2·74 2·40	Orange
$\{Fe(dppd)_2\}_n$	1·45	2·29	Violet
$\{Fe(pbd)_2\}_n$	1·44	2·38	Black

pd = Pentane-2,4-dionate, dppd = 1,3-diphenylpropane-1,3-dionate, pbd = 1-phenylbutane-1,3-dionate, sala = salicylaldehydate, pip = piperidine, and py = pyridine.

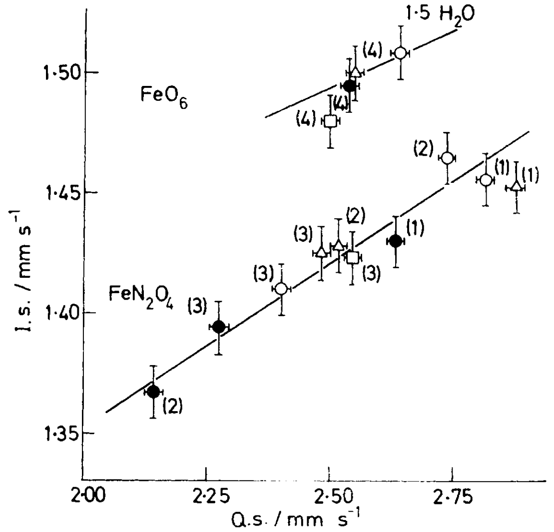


FIGURE 1 Isomer shift and quadrupole-splitting values of $[Fe(L_2)L'_2]$ chelate complexes measured at 95 K: L = pd (○), dppd (●), pbd (△), and sala (□); L′ = NH_3 (1), pip (2), py (3), and H_2O (4)

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[5] (*a*) R. Nast and H. Rückemann, *Chem. Ber.*, 1960, **93**, 2329; (*b*) *Z. anorg. Chem.*, 1961, **307**, 309; (*c*) D. A. Buckingham, J. L. E. Cheong, J. E. Ferguson, and C. J. Wilkins, *J. Chem. Soc.*, 1963, 3461.

[6] Y. Takashima, T. Hanamura, and Y. Maeda, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2101.

polymeric structure, which indeed has been reported for the complex [Fe(pd)] (pd = pentane-2,4-dionate).[5c] For the latter complex, generally two different quadrupole pairs were observed, both characteristic of Fe^{II}, which may be ascribed to two polymeric species. Six-co-ordination is also probable in the complex $[Fe(pd)_2]$,$1{\cdot}5H_2O$ which has been prepared previously.[7] Only one q.s. was observed for this complex which excludes the possibility of a mixture of $[Fe(pd)_2]$ and $[Fe(pd)_2]$,$2H_2O$. Most chelate complexes of this series did not show any band in the i.r.–visible region that can be ascribed to an electronic *d–d* transition. The complexes $[Fe(pd)_2]$ and $[Fe(dppd)_2]$ showed one band at 8 900 cm^{-1} on the edge of an intense charge-transfer (c.t.) band; this band disappeared on oxidation of the complexes. Comparison with the spectrum of the ion $[Fe(H_2O)_6]^{2+}$ suggests that the observed band is attributable to one of the two ${}^5E_g \leftarrow {}^1T_{2g}$ transitions, the other band being hidden under the c.t. band.[8]

Chelate Complexes with Bidentate Schiff Bases [*Ligands* (III)].—Mössbauer parameters measured for $[Fe(Rsal)_2]$ and $[Fe(Rsal)_2(py)_2]$ complexes (R = *N*-alkylsalicylideneiminate, py = pyridine) are given in Table 2. Except for R = Pr^i and Bu^t the influence of R on Mössbauer parameters of the complexes $[Fe(Rsal)_2]$ is small. The similarity between the parameters of $[Fe(Rsal)_2]$ and those of $[Fe(Rsal)_2(py)_2]$ suggests six-co-ordination for iron in all these complexes. This can be achieved by polymerization, as has been observed for Schiff-base complexes of other metals.[1b] Six-co-ordination is very common for high-spin iron(II) bound to oxygen and nitrogen atoms; in the $[Fe(Rsal)_2]$ complexes it may occur through formation of Fe–O–Fe bonds, using lone-pair electrons of the oxygen atoms.

TABLE 2

Mössbauer parameters (mm s^{-1}) and electronic-transition energies ($E_{d\text{–}d}$/cm^{-1}) of iron(II) chelate complexes with bidentate Schiff bases, measured at 95 K

	I.s.	Q.s.	$E_{d\text{–}d}$	Colour
$[Fe(Mesal)_2]$	1·34	2·19	9 500 ± 300	Red
$[Fe(Etsal)_2]$	1·33	2·11	9 300 ± 400	Red
$[Fe(Pr^nsal)_2]$	1·32	2·06	8 800 ± 200	Red
$[Fe(Bu^nsal)_2]$	1·34	2·09	9 000 ± 600	Red
$[Fe(Bu^isal)_2]$	1·34	2·08	8 800 ± 600	Red
$[Fe(Pr^isal)_2]$	1·13	1·54	9 050 ± 200 12 150 ± 200	Ochre
$[Fe(Bu^tsal)_2]$	1·13	1·76		Brownish red
$[Fe(Mesal)_2(py)_2]$	1·31	2·26		Black
$[Fe(Etsal)_2(py)_2]$	1·34	2·22		Black
$[Fe(Pr^nsal)_2(py)_2]$	1·35	2·28		Black
$[Fe(Bu^nsal)_2(py)_2]$	1·34	2·29		Black
$[Fe(Bu^isal)_2(py)_2]$	1·37	2·20		Black
$[Fe(Pr^isal)_2(py)_2]$	1·39	2·13		Black
$[Fe(Bu^tsal)_2(py)_2]$	1·41	2·17		Black

Mesal, Etsal, Pr^nsal, Pr^isal, Bu^nsal, Bu^isal, and Bu^tsal = *N*-Methyl-, *N*-ethyl-, *N*-propyl-, *N*-(i-propyl)-, *N*-butyl-, *N*-(i-butyl)-, and *N*-(t-butyl)] salicylideneiminate.

The Mössbauer spectrum of the complex $[Fe(Etsal)_2]$ at 4·2 K (Figure 2) displayed large asymmetry. This asymmetry is not due to the Goldanskii–Karyagin effect [3c] since it disappeared with increasing temperature and thus is probably due to relaxation effects. Several $[Fe(Rsal)_2]$ complexes showed a clear electronic band

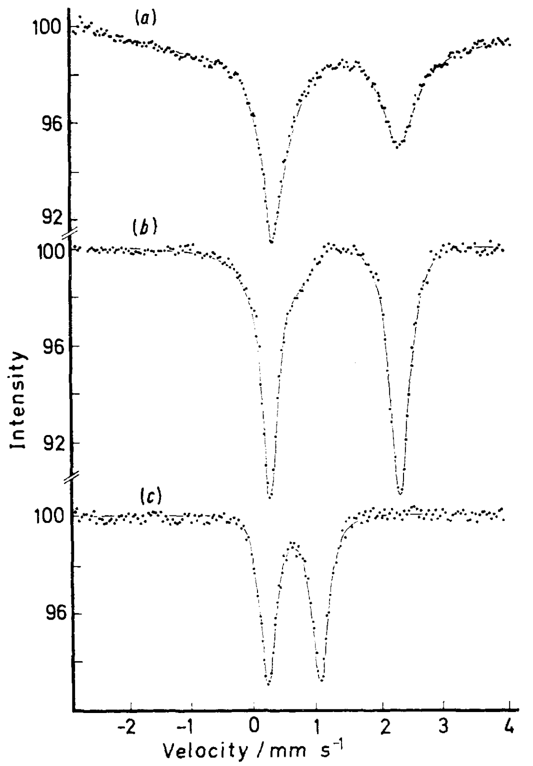

FIGURE 2 Mössbauer spectra of the complex $[Fe(Etsal)_2]$ at (*a*) 4·2, (*b*) 85, and (*c*) 85 K after exposure to air

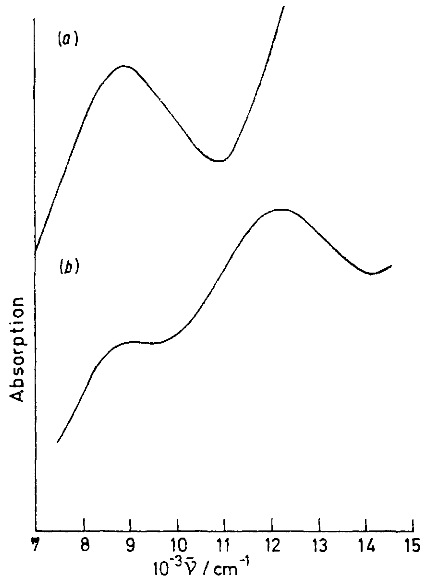

FIGURE 3 Electronic spectra of the complexes $[Fe(Pr^nsal)_2]$, (*a*), and $[Fe(Pr^isal)_2]$, (*b*), measured in KBr disks

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[7] B. Emmert and R. Jarczynski, *Ber.*, 1931, **64**, 1072.

[8] F. A. Cotton and M. D. Meyers, *J. Amer. Chem. Soc.*, 1960, **82**, 5023.

below 12 000 cm^{-1} (see Figure 3 and Table 2). As in the previous section, we ascribe this band to one of the $^5E_g \leftarrow {}^5T_{2g}$ transitions, and assume again that the second band is masked by the much more intense c.t. bands above 10 000 cm^{-1}. Fortunately this assumption is supported by the [Fe(Pr^{i}sal)$_2$] spectrum, in which both *d–d* bands were seen clearly due to the absence of c.t. bands in this region. These electronic spectra are characteristic for high-spin six-co-ordinate iron(II) and thus confirm the proposed six-co-ordination of iron. For R = Pr^i and Bu^t this conclusion might seem surprising: nickel chelate complexes with these ligands contain tetrahedrally co-ordinated nickel, while for all the other R groups planar geometry is observed.[9] The low i.s. values of these two complexes are compatible with a lower co-ordination number. However, the values of the observed electronic-transition energies exclude tetrahedral co-ordination. The low i.s. value might be caused by distortion of the complex by the bulky Pr^i and Bu^t groups, resulting in occupied 3*d* orbitals of iron being mixed with empty 4*s* orbitals. As a result some electronic charge may be transferred from the 3*d* to 4*s* orbitals, which might explain the small i.s. values as well as the deviating q.s.'s.

Chelate Complexes of Quadridentate Schiff Bases [*Ligands* (IV)].—Again the Mössbauer parameters measured (see Table 3) were very similar to those found for the [Fe(Rsal)$_2$] complexes and the adducts, which suggests that even in these complexes iron is six-co-ordinated. Square-planar geometry, favoured by the quadridentate ligands, is expected to give rise to a smaller i.s. and a very large q.s. From magnetic susceptibilities of [Fe(pnsal)$_2$] and [Fe(ensal)], Earnshaw *et al.*[10] concluded that both complexes have four unpaired electrons and a highly distorted symmetry. We conclude that in iron chelate complexes with quadridentate Schiff bases polymerization occurs, leading to six-co-ordination of the iron atom. This is in agreement with the conclusions of Fitzsimmons *et al.*[4] concerning the complexes [Fe(ensal)] and [Fe(phnsal)]. In the electronic spectra, strong broad bands were observed that disappeared after exposure of the sample to air (see Figure 4). The bands occurred at low energies (*ca.* 6 500 cm^{-1}, see Table 3) close to the absorption range characteristic of tetrahedral co-ordination; however, for the complex [Fe(bnsal)] a second band at 11 900 cm^{-1} was observed and therefore we ascribe all bands to $^5E_g \leftarrow {}^5T_{2g}$ transitions as in the case of [Fe(Rsal)$_2$].

TABLE 3

Mössbauer parameters (mm s^{-1}) and electronic-transition energies (E_{d-d}/cm^{-1}) of iron(II) complexes with quadridentate Schiff bases, measured at 95 K

	I.s.	Q.s.	E_{d-d}	Colour
[Fe(ensal)]	1·29	2·48	6 100	Lilac
[{Fe(ensal)}$_2$(en)]	1·27	2·26		
[Fe(pnsal)]	1·30	2·42	5 700	Red
[Fe(bnsal)]	1·37	2·32	7 550 11 900	Red
[Fe(phnsal)],H_2O	1·29	2·41	6 450	Green
[Fe(ensal)(py)$_2$]	1·222	2·09		Black
[Fe(pnsal)(py)$_2$]	1·366	2·43		Black
[Fe(phnsal)(py)$_2$]	1·297	1·99		Black

ensal, pnsal, bnsal, and phnsal = *NN'*-Ethylene-, *NN'*-propylene-, *NN'*-butylene-, and *NN'*-*o*-phenylene-bis(salicylideneiminate).

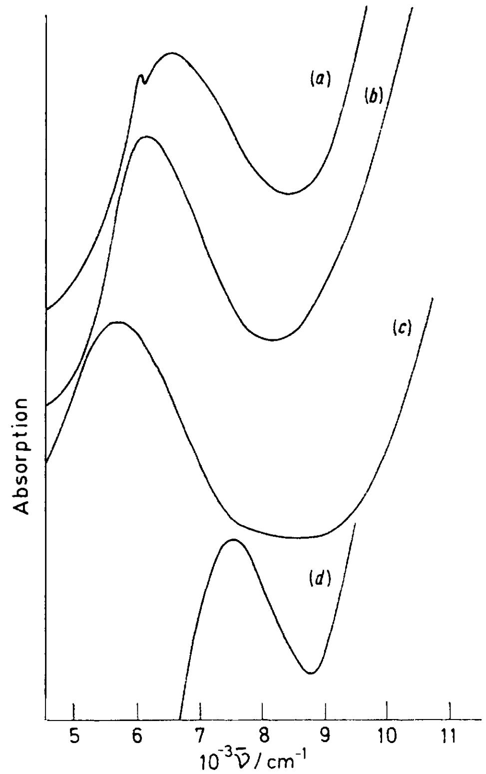

FIGURE 4 Electronic spectra of the complexes [Fe(phnsal)], (*a*), [Fe(ensal)], (*b*), [Fe(pnsal)], (*c*), and [Fe(bnsal)], (*d*) measured in KBr disks

The Chemical Bonding.—In Figure 1 two groups of complexes can be discerned, namely one group in which iron is bound to six oxygen atoms (denoted FeO_6) and a second group where iron is bound to four oxygen and two nitrogen atoms (denoted FeN_2O_4). The separation into two groups indicates that the i.s. is mainly determined by atoms bound directly to the iron atom. Since generally i.s. decreases with increasing covalency, it can be seen that the acac complexes are more ionic than those of dbm, and that ionicity in the Fe–L' bonds decreases in the order $H_2O > NH_3 >$ pip > py (pip = piperidine). The most striking result in Figure 1 is the i.s.–q.s. relation observed for the FeN_2O_4 complexes: this relation suggests that all the complexes involved have considerable similarity in their molecular structure. If a ligand L' on the *z* axis was replaced by a ligand having more covalent character both the i.s. and the q.s. decreased. The latter means that a more spherical charge distribution is reached, from which it can be

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[9] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1963, **2**, 181; L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, 1963, **85**, 411.

[10] A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1968, 1048.

concluded that the bidentate ligands are more strongly bound to iron than the unidentate ligands. As a consequence the metal $3d_{z^2}$ orbital lies lower than the $3d_{x^2-y^2}$, and $3d_{xz}$, $3d_{yz}$ lie lower than $3d_{xy}$. For the complexes studied here σ-bonding is the dominating bonding mechanism. Even in the py complexes, interaction between the π-orbitals of py and the metal 3*d* orbitals is small.[11] Since π-bonding increases according to the spectrochemical series, all other ligands discussed here are expected to have even less π-bonding than py. The small importance of π-bonding, even in iron–sulphur bonds, is illustrated by results from extended-Hückel calculations on iron dithiocarbamate complexes.[12]

In Figure 5 the temperature dependence of i.s. and q.s. for the complexes $[Fe(pd)_2L_2']$ is shown. The decrease of i.s. with temperature can be explained by the influence of the second-order Doppler effect [13] (*ca.* 0·06 mm s^{-1} over 100 K). The temperature dependence of q.s. is related to the presence of excited states which are thermally accessible. The structures of the pd complexes can be considered as octahedrons, with rhombic distortion. The effect of the rhombic crystal field and spin–orbit coupling on the iron T_{2g} level can be described by the Hamiltonian in equation (1),[14] where δ and ε are

$$\mathscr{H} = -\lambda LS - \delta(\mathrm{L}_z^2) - \tfrac{\varepsilon}{4}(L_+^2 + L_-^2) \qquad (1)$$

the axial and rhombic crystal-field parameters, respectively, λ is the spin–orbit coupling constant, and *L* and *S* are the orbital and spin momentum operators, respectively. Using this Hamiltonian, Ingalls,[14] followed by many others,[15] calculated the temperature dependence of the q.s. as a function of δ and ε. The effect of covalency is usually taken into account through an orbital correction factor α^2,[14] reflecting the effect of covalency on the expectation value $\langle r^{-3}\rangle$ for T_{2g} electrons and on the value of λ. However, because of the dominance of σ-bonding, covalency effects can be expected to be much more important for the metal E_g levels. These effects can contribute to the q.s. because the population numbers a^2 and b^2 of the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals may be different, resulting in a contribution to the *z* component, V_{zz}, of the electric-field gradient (e.f.g.) given by equation (2), where R_{3d} is a shielding factor. This

$$V_{zz}^{\mathrm{cov}} = \frac{4}{7}\,\frac{e}{4\pi\varepsilon_0}\,\langle r^{-3}\rangle_{3d}\,(1 - R_{3d})(b^2 - a^2) \qquad (2)$$

temperature-independent contribution in general reduces the q.s. due to the T_{2g} electrons, in much the same way as the lattice contribution to the e.f.g. We calculated q.s.(*T*) as function of δ, ε, α^2, and $(b^2 - a^2)$. A typical plot is shown in Figure 6, where q.s. at 90 K is given as a function of δ and ε for $\alpha^2 = 1$ and for two different values of $(a^2 - b^2)$.

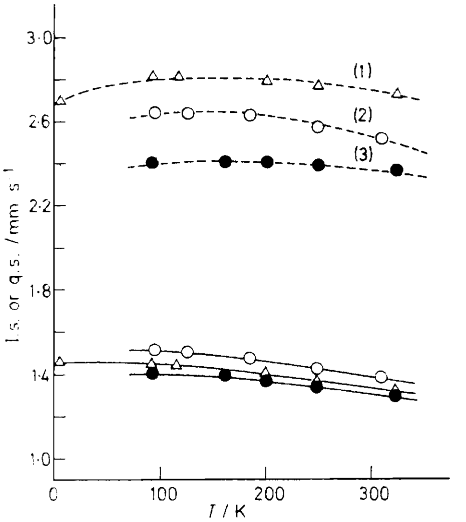

FIGURE 5 Experimental i.s. (lower) and q.s. values (upper) for three $[Fe(pd)_2L'_2]$ complexes: L′ = H_2O (○); NH_3 (△); and py (●). (— — —), Calculated q.s. (*T*) curves for: δ = −15, ε = 8, $(a^2 - b^2)$ = 0·15, and α^2 = 0·85 (1); δ = −30, ε = 7, $(a^2 - b^2)$ = 0·25, and α^2 = 0·83 (2); and δ = −10, ε = 8, $(a^2 - b^2)$ = 0·05, and α^2 = 0·70 (3). δ and ε are expressed in units of |λ|

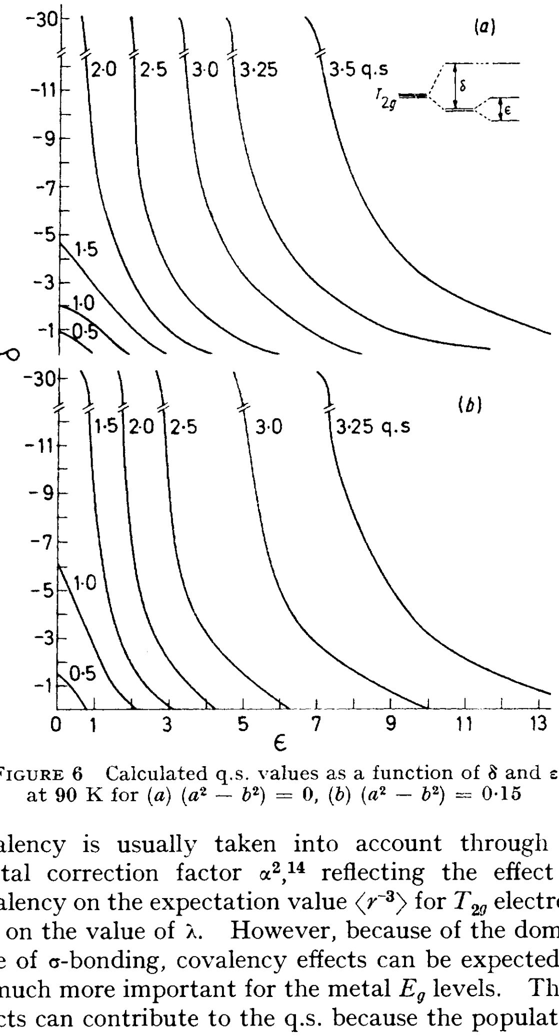

FIGURE 6 Calculated q.s. values as a function of δ and ε at 90 K for (*a*) $(a^2 - b^2) = 0$, (*b*) $(a^2 - b^2) = 0·15$

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[11] C. K. Jørgensen, ' Inorganic Complexes,' Academic Press, London, 1963, p. 70.

[12] J. L. K. F. de Vries, C. P. Keijzers, and E. de Boer, *Inorg. Chem.*, 1972, **11**, 1343.

[13] A. A. Maradudin, P. A. Flinn, and S. Ruby, *Phys. Rev.*, 1962, **126**, 9.

[14] R. Ingalls, *Phys. Rev.*, 1964, **133**, A787.

[15] T. C. Gibb and N. N. Greenwood, *J. Chem. Soc.*, 1965, 6989; R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, 1966, **62**, 1713; R. M. Golding, *Mol. Phys.*, 1967, **12**, 13; T. C. Gibb, *J. Chem. Soc.* (*A*), 1968, 1439; J. C. Travis, 'An Introduction to Mössbauer Spectroscopy,' ed. L. May, Plenum Press, New York, 1971, ch. 4.

In fitting an experimental q.s.(T) curve with calculated curves, generally no unique set of parameters can be found. In Figure 5 the broken curves represent computed q.s.(T) curves for parameters listed in the Figure caption and experimental data for three pd complexes are seen to lie on these curves. The choice of this set of parameters was based on the following considerations: the rhombic-splitting parameter ε should be about the same for all three pd-complexes studied; and the parameters δ, α^2, and $(a^2 - b^2)$ should all roughly increase on going from py to NH_3 to H_2O. Using $\alpha^2|\lambda|$ as the spin-orbit coupling constant in these complexes ($\lambda = 104$ cm^{-1} for free Fe^{2+}), we found $\varepsilon = 600 \pm 100$ cm^{-1} and that δ is negative and may vary from 1 000 cm^{-1} to several thousand cm^{-1} without affecting q.s. very much. This means that all the chelate complexes studied have strong axial distortion and moderate distortion in the xy plane. This conclusion is in agreement with Takashima's results on some dppd complexes.[6] For $\delta > 0$, calculated q.s.(T) curves strongly depended on δ and no set of parameters fitting the experimental curves was found. The negative value of δ confirms our statement at the beginning of this section that the $3d_{z^2}$ orbital lies lower than $3d_{x^2-y^2}$ and $3d_{xz}$, $3d_{yz}$ lower than $3d_{xy}$. In chemical terms it means that the two unidentate ligands have smaller bond strength than the bidentate ligands. For chelate complexes of Schiff bases the experimental q.s.(T) curve was essentially the same as for the pd complexes; because of the probably lower symmetry, no complete fitting was attempted, but the small q.s. variations suggest again large axial distortions. When both bands are visible, the splittings between the bands in the electronic spectra similarly suggest large splittings between the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals. Since in chelate complexes with quadridentate ligands these splittings are very large, the bond strength seems to increase on going from unidentate to bidentate to quadridentate ligands. It can thus be understood why q.s.'s of all neutral chelate complexes published so far [16] are within a relatively small range {2·0—2·9 mm s^{-1}, except for [Fe(Pr^{i}sal)$_2$] and [Fe(Bu^{t}sal)$_2$]}. This range seems to be characteristic for neutral high-spin iron(II) chelate complexes, since in general q.s's of such complexes are very sensitive to chemical variations and vary almost continuously between 0 and 4 mm s^{-1}.

EXPERIMENTAL

The chelate complexes were prepared in vacuum with the use of an apparatus described elsewhere.[17] Metal salt and ligand solutions were degassed thoroughly, and after mixing both solutions the chelate complexes were formed immediately. The products were washed in the apparatus with previously degassed water, and dried by distilling off the solvent. Samples were prepared in a VAC HE-43-6 glove-box with HE-373 dritrain; for the Mössbauer measurements the solid was sealed in a polypropylene capsule, while for electronic spectra a KBr pellet was pressed in the absence of air. No relevant data could be obtained from solution spectra, since on dissolving undesired reactions might occur. Mössbauer spectra were measured with a spectrometer of the constant-acceleration type, described elsewhere; [17] ^{57}Co in palladium was used as the source. For the velocity calibration an iron-metal foil was used. Spectra could be measured at various temperatures down to 4 K, the temperature being kept constant within 1 K. For recording electronic spectra in the 4 000—16 000 cm^{-1} range, use was made of a Cary 14 instrument.

Preparations.—The complexes [Fe(L$_2$)L$_2$′] [L = *β-diketonate*, (I), *or salicylaldehydate*, (II); L′ = H_2O, NH_3, *pyridine* (py), *or piperidine* (pip)]. For L′ = py, pip, or NH_3, in general an iron(II) sulphate solution was allowed to react with a solution of the pure ligand in the presence of excess of base (L′).[7,18] These preparations were carried out in a nitrogen atmosphere, since in vacuum the unidentate ligand L′ was partially removed. The complexes with L′ = H_2O were prepared in vacuum, as described above; the sodium salt of the ligand was preferred as a starting material in this case {Found: C, 43·7; H, 6·2. [Fe(pd)$_2$],1·5H_2O requires C, 42·7; H, 6·1. Found: C, 57·6; H, 5·9; N, 6·9. [Fe(pd)$_2$(py)$_2$] requires C, 58·3; H, 5·9; N, 6·8. Found: C, 66·6; N, 4·8. [Fe(dppd)$_2$(H_2O)$_2$] requires C, 66·9; H, 4·9. Found: C, 66·9; H, 5·3; N, 4·8. [Fe(dppd)$_2$(en)] requires * C, 68·1; H, 5·7; N, 5·0. Found: C, 65·0; H, 6·4; N, 4·1. [Fe(dppd)$_2$(pip)$_2$] requires C, 64·1; H, 6·2; N, 3·9. Found: C, 72·4; H, 5·0; N, 4·2. [Fe(dppd)$_2$(py)$_2$] requires C, 72·1; H, 4·9; N, 4·2. Found: C, 50·7; H, 4·4. [Fe(sala)$_2$(H_2O)$_2$] requires C, 50·4; H, 4·2. Found: C, 46·6; H, 5·1. [Fe(pd)$_2$] requires C, 47·3; H, 5·6. Found: C, 70·5; H, 4·5. [Fe(dppd)$_2$] requires C, 71·1; H, 4·4%}.

Chelate complexes with N-*alkylsalicylideneiminates*, (III). Schiff bases (III) were formed by reaction of salicylaldehyde and primary amines (RNH_2). Iron(II) *N*-alkylsalicylideneiminate complexes, [Fe(Rsal)$_2$], were prepared by mixing stoicheiometric amounts of iron(II) acetate and ligands (III) in ethanol solution.[4,17] The brightly coloured precipitates were washed with water; investigation of the washings afterwards confirmed that 2 : 1 complexes [Fe(Rsal)$_2$] were formed. Elemental analyses showed that most [Fe(Rsal)$_2$] samples did not contain solvent molecules. No satisfactory preparation method could be found for R = H or R = OH; Mössbauer spectra of the complexes indicated iron coordination by six oxygen atoms. Bis(pyridine) adducts of [Fe(Rsal)$_2$] were formed by using py as solvent instead of water. These black complexes are rather stable in air, as could be seen from the Mössbauer spectra {Found: C, 56·4; H, 4·6; Fe, 17·5; N, 7·8. [Fe(Mesal)$_2$] requires C, 59·3; H, 5·0; Fe, 17·2; N, 8·6. Found: C, 59·3; H, 5·5; Fe, 15·3; N, 7·6. [Fe(Etsal)$_2$] requires C, 61·4; H, 5·7; Fe, 15·9; N, 8·0. Found: C, 63·4; H, 6·3; N, 7·6. [Fe(Pr^{n}sal)$_2$] requires C, 63·2; H, 6·4; N, 7·4. Found: C, 67·4; H, 7·4; N, 7·0. [Fe(Bu^{n}sal)$_2$] requires C, 64·8; H, 6·9; N, 6·9. Found: C, 64·9; H, 6·5; N, 7·7. [Fe(Pr^{i}sal)$_2$] requires C, 63·2; H, 6·4; N, 7·4. Found: C, 66·1; H, 7·0; N, 6·9. [Fe(Bu^{i}sal)$_2$] requires C, 64·8; H, 6·9; N, 6·9%}.

Chelate complexes of NN′-*ethylenebis*(*salicylideneiminate*) *and related ligands*, (IV). The ligands (IV) were prepared by reaction of salicylaldehyde and the appropriate diamine. The preparation procedure for the complexes was similar

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* en = Ethylenediamine.

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to that used above. When a water–ethanol mixture was used as solvent the [Fe(phnsal)] complex was isolated as a monohydrate; the water molecule is probably not bound to the iron atom, as indicated by the slight change in the Mössbauer spectrum on removal of the water {Found: C, 59·6; H, 4·3; N, 8·9. [Fe(ensal)] requires C, 59·6; H, 4·4; N, 8·7. Found: C, 57·0; H, 4·7; N, 10·6. [{Fe(ensal)}$_2$(en)] requires C, 58·4; H, 4·6; N, 11·9. Found: C, 61·0; H, 5·0; N, 9·0. [Fe(pnsal)] requires C, 60·7; H, 4·8; N, 8·3. Found: C, 62·0; H, 5·5; N, 8·6. [Fe(bnsal)] requires C, 61·7; H, 5·2; N, 8·0. Found: C, 60·7; H, 4·0; N, 7·1. [Fe(phnsal)] requires C, 61·9; H, 4·1; N, 7·2%}. After recrystallization in air the following complexes were also obtained [Found: C, 58·1; H, 4·3; N, 8·6. {Fe(ensal)}$_2$O requires C, 58·2; H, 4·3; N, 8·5. Found: C, 63·7; H, 4·0; N, 7·6. {Fe(phnsal)}$_2$O requires C, 63·7; H, 3·7; N, 7·4%].

We thank Miss M. Koning for her assistance in preparation of the iron complexes, Mr. J. Diersmann for carrying out elemental analyses, and the Netherlands Foundation for Chemical Research and the Netherlands Organization for Pure Research for support.

[4/239 *Received, 7th February,* 1974]