

The Strengths of Bonding and Degree of Distortion from Octahedral Symmetry by Mössbauer Spectroscopy

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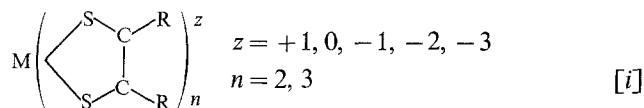
The use and the limitations of Mössbauer quadrupole splittings in the differential analysis of iron(II) and iron(III) in strong field complexes is investigated. By way of example, some literature Mössbauer data on dithiolene complexes of iron are interpreted in terms of the environment of the iron atom. In the six-coordinated complexes, there is considerable distortion from octahedral symmetry (corresponding to $3\delta \sim 1200 \text{ cm}^{-1}$). In the five-coordinated complexes, the distortion is also large (corresponding to $3\delta \sim 2200 \text{ cm}^{-1}$), and the values of the ratio, β/α , of the molecular orbital coefficients are found to follow the trend that would be expected from the usual bond strengths of the various ligands.

Die Grenzen in der Anwendung der Mössbauer-Quadrupol-Aufspaltung in der Differentialanalyse von Fe(II) und Fe(III) in Komplexen mit starken Feldern werden untersucht. Der Einfluß der Umgebung des Eisenatoms wird zur Deutung von Mössbauer-Daten von Dithiolenenkomplexen des Eisens herangezogen. In den sechsfach koordinierten Komplexen liegt eine beträchtliche Störung der Oktaedersymmetrie vor ($3\delta \sim 1200 \text{ cm}^{-1}$). Ebenso ist die Störung in fünffach koordinierten Komplexen erheblich ($3\delta \sim 2200 \text{ cm}^{-1}$). Die Werte für das Verhältnis der MO-Koeffizienten β/α liegen in einem Bereich, den man für die üblichen Bindungsstärken der verschiedenen Liganden erwartet.

Etude de l'utilisation des couplages quadrupolaires Mössbauer dans l'analyse différentielle des fers II et III dans des complexes à champ fort. A titre d'exemple on interprète en terme d'environnement de l'atome de fer certaines données de la littérature sur l'effet Mössbauer dans les complexes dithiolene Fer. Dans les complexes hexacoordinnés on s'écarte considérablement de la symétrie octaédrique (distortion correspondant à $3\delta \approx 1200 \text{ cm}^{-1}$). Dans les complexes pentacoordinnés, la distortion est aussi importante (correspondant à $3\delta \approx 2200 \text{ cm}^{-1}$) et les valeurs des rapports β/α des coefficients des orbitales moléculaires suivent la loi à laquelle on peut s'attendre d'après les forces de liaisons usuelles des différents ligands.

Introduction

The chemistry of 1,2-dithiolene chelate transition metal iron compounds has recently been of much interest [1]. Complex anions and cations [*i*] of variable electronic charge are formed and



experimental investigations have included the Mössbauer spectra of a series of anionic and neutral iron complexes [2] (Table 1).

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Table 1. Mössbauer data for some iron 1,2-dithiolenes

Complex	Structure	Isomer shift		Quadrupole splitting	
		(mm/sec)		(mm/sec)	
		77° K	295° K	77° K	295° K
<i>Group A</i>					
(1) [(C ₆ H ₅) ₄ P] ₂ [FeS ₆ C ₆ (CN) ₆]	6-coordinate	0.50	0.42	1.57	1.59
(2) [(C ₆ H ₅) ₄ P] ₃ [FeS ₆ C ₆ (CN) ₆]	6-coordinate	0.65	—	1.69	—
<i>Group B</i>					
(3) [(C ₂ H ₅) ₄ N][FeS ₄ C ₄ (C ₆ H ₅) ₄]	5-coordinate dimer	0.61	0.53	2.37	2.45
(4) [(C ₂ H ₅) ₄ N][FeS ₄ C ₄ (CN) ₄]	5-coordinate dimer	0.59	0.50	2.76	2.81
<i>Group C</i>					
(5) [(C ₆ H ₅) ₄ P][Fe(pyridine)S ₄ C ₄ (CN) ₄]	5-coordinate pyridine adduct	0.59	0.53	2.41	2.51
<i>Group D</i>					
(6) [(C ₆ H ₅) ₄ P][Fe(NO)S ₄ C ₄ (CN) ₄]	5-coordinate NO adduct	0.31	0.20	1.68	1.69
(7) [(C ₆ H ₅) ₄ P] ₂ [Fe(NO)S ₄ C ₄ (CN) ₄]	5-coordinate NO adduct	0.47	—	0.97	—
(8) [Fe(NO)S ₄ C ₄ (C ₆ H ₅) ₄]	5-coordinate NO adduct	0.32	0.24	1.65	1.65
(9) [(C ₂ H ₅) ₄ N][Fe(NO)S ₄ C ₄ (C ₆ H ₅) ₄]	5-coordinate NO adduct	0.27	0.20	1.98	1.99

Some of these (2, 3, 4, 5, 8) are formally iron (III) complexes, some (6, 9) iron (II), and (1) and (7) are formally iron (IV) and iron (I) respectively. Moreover, the entire range of formal oxidation numbers 0, I, II, III, IV has already been observed [3, 4] in iron dithiolenes, and it is obvious that the oxidation numbers are not a meaningful concept, since they provide no information about the number of 3*d* electrons associated with the central metal atoms. The excess or deficiency of electrons in some of the complexes is associated mainly with the ligands, and when larger and better electron acceptors such as porphyrins are used as ligands, an even greater range of oxidation states is obtainable. In such cases, Mössbauer results, which depend on the electronic configuration near the iron nucleus, have a distinct advantage over magnetic susceptibility measurements, where the results depend on the electronic configuration of the entire molecule.

The electronic structures of the various dithiolenes are not known, and the range of results of physical measurements available is rather incomplete at present. We will show that the Mössbauer data are adequately explained in terms of a 3*d*⁵ system in a strong crystal field, involving considerable molecular orbital overlap with the ligands, and distortion from cubic symmetry, although, in a couple of cases it is difficult to distinguish between the low spin 3*d*⁵ and low spin 3*d*⁶ configurations from the Mössbauer isomer shifts and the temperature dependence of the quadrupole splitting. We will suggest other physical measurements to further develop this hypothesis.

Theory

The isomer shifts observed for the compounds in Table 1 are of the magnitude expected for low spin iron (III), and it is therefore reasonable to apply the recently developed theory for the temperature dependence of the quadrupole splitting ΔE_Q of low spin ferric compounds [5, 6]. The expected isomer shifts for low spin iron (II) and iron (III) are very similar [6] and consequently we shall also consider the possibility of a $3d^6$ configuration. Normally, the two cases can be differentiated by the temperature dependence of ΔE_Q in iron (III) and its temperature independence in iron (II) compounds [6]. We shall show that ΔE_Q may be temperature independent over the temperature range of interest in certain compounds for both types.

Iron (III)

In a strong crystal field of octahedral symmetry the electronic ground state of the Fe^{3+} ion is the 2T_2 state. The quadrupole splitting for such an ion is zero. However, any distortion from octahedral symmetry will give rise to a non-zero quadrupole splitting. If the covalency effects are ignored and the degree of distortion expressed by a distortion parameter δ , then the appropriate Hamiltonian [5] may be written, in the usual notation, as

$$\mathcal{H} = \sum_i \left[\zeta l_i \cdot s_i + \delta l_{iz}^2 + \frac{e^2 Q' \langle r^{-3} \rangle}{7I(I+1)} \left\{ (l_i \cdot I)^2 + \frac{1}{2} (l_i \cdot I) - 2I(I+1) \right\} \right]. \quad (1)$$

Operating with (1) on the basic 2T_2 wavefunctions $|1\rangle$, $|-1\rangle$ and $|\zeta_1\rangle$ to obtain the non-negligible elements $\langle \psi M_I' | \mathcal{H} | \psi M_I \rangle$, yields the quadrupole splitting:

$$\Delta E_Q = \frac{e^2 Q' \langle r^{-3} \rangle}{14} \frac{\sum_n A_n \exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)} \quad (2)$$

where

$$\begin{aligned} E_1 &= - \left\{ \frac{1}{4} + \frac{x}{2} + \frac{X}{2} \right\} \zeta, \\ A_1 &= 1 - 3 \left(\frac{1}{2} - 3x \right) X^{-1}, \\ E_2 &= - \left\{ \frac{1}{4} + \frac{x}{2} - \frac{X}{2} \right\} \zeta, \\ A_2 &= 1 + 3 \left(\frac{1}{2} - 3x \right) X^{-1}, \\ E_3 &= \left\{ \frac{1}{2} + x \right\} \zeta, \\ A_3 &= -2. \end{aligned}$$

In Eq. (2) $Q' = Q(1 - \gamma_\infty)$, Q is the nuclear quadrupole moment, γ_∞ is the Sternheimer screening factor [7] and ζ is the spin-orbit coupling constant. $X^2 = \frac{9}{4} - 3x + 9x^2$ and $x = \delta/\zeta$. The splitting of the 2T_2 state is 3δ . Such a distortion effect was taken into account in a group of ferric dithiocarbamates [8], and there the deviation from octahedral symmetry was found to be small.

In real complexes, the metal orbitals may deviate from d -orbital character due to bonding overlap with the ligands, and in the general case, the bonding effects will be different in different directions. In such complexes as the dithiolenes, these bonding effects are likely to be considerable. In the calculations, the atomic orbital wavefunctions $|1\rangle$, $|-1\rangle$ and $|\zeta_1\rangle$ must be replaced by the molecular orbitals

$$\alpha|1\rangle + \phi_1, \alpha|-1\rangle + \phi_2 \quad \text{and} \quad \beta|\zeta_1\rangle + \phi_3 \quad (3)$$

where the ϕ_1 , ϕ_2 and ϕ_3 are appropriate ligand orbitals. The coefficients α , β (< 1) tend to unity as bonding effects decrease. The quadrupole splitting is now given by

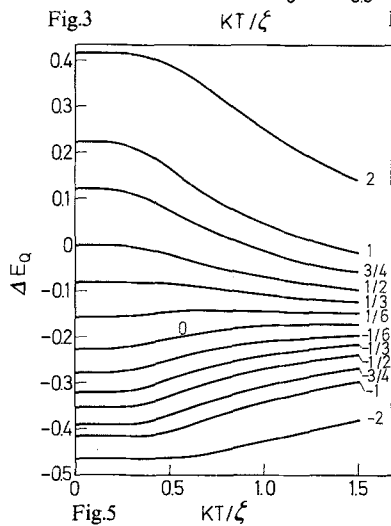
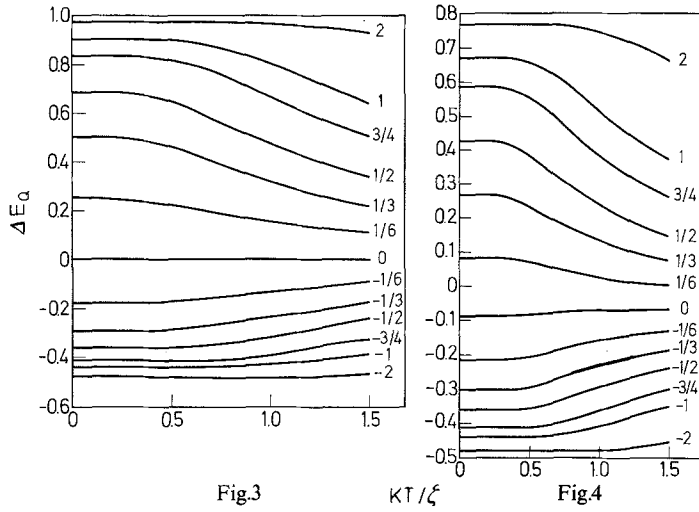
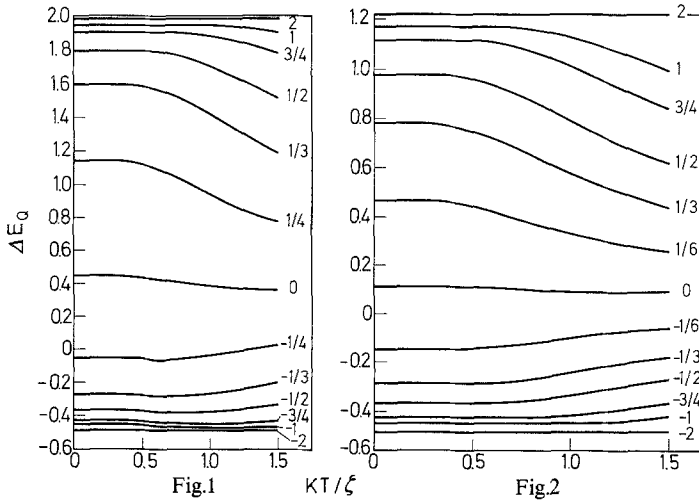
$$\Delta E_Q = \frac{2}{7} e^2 Q' \langle r^{-3} \rangle \alpha^2 \left\{ \frac{A_1 \exp(-E_1/kT) + A_2 \exp(-E_2/kT) + A_3 \exp(-E_3/kT)}{\exp(-E_1/kT) + \exp(-E_2/kT) + \exp(-E_3/kT)} \right\} \quad (4)$$

where

$$\begin{aligned} E_1 &= -\{1/4 - (1 - 4\beta^2/\alpha^2)x/6 + X/2\} \zeta', \\ A_1 &= b^2 \beta^2/\alpha^2 - a^2/2, \\ E_2 &= -\{1/4 - (1 - 4\beta^2/\alpha^2)x/6 - X/2\} \zeta', \\ A_2 &= a^2 \beta^2/\alpha^2 - b^2/2, \\ E_3 &= \{1/2 - (1 - 4\beta^2/\alpha^2)x/3\} \zeta', \\ A_3 &= -1/2, \\ X^2 &= 2\beta^2/\alpha^2 + 1/4 + (1 - 4\beta^2/\alpha^2)x + (1 - 4\beta^2/\alpha^2)^2 x^2, \\ a^2 &= 1/2 + 1/2\{1/2 + (1 - 4\beta^2/\alpha^2)x\} X^{-1}, \\ b^2 &= 1/2 - 1/2\{1/2 + (1 - 4\beta^2/\alpha^2)x\} X^{-1}, \\ \zeta' &= \alpha^2 \zeta. \end{aligned}$$

The dependence of the $\Delta E_Q(T)$ curve on the value of δ/ζ when $\alpha = \beta$ has been described [5]. The effect of various ratios of $\alpha : \beta$ is shown in Figs. 1-5.

The g -tensor observed in a paramagnetic complex is a function of the environment of the paramagnetic metal atom, and in the case of potassium ferricyanide, it has been used to obtain ΔE_Q as a function of ζ' , $e^2 Q' \langle r^{-3} \rangle$ and temperature [5]. Using the free ion value of 400 cm^{-1} for ζ , and the value of 278 cm^{-1} obtained from the magnetic susceptibility for ζ' , and comparing with the observed $\Delta E_Q(T)$ curve, values of 0.7, and 8.9 mm/sec were obtained for α^2 and $e^2 Q' \langle r^{-3} \rangle$ respectively. Because of the equivalence of the six ligands, $\alpha = \beta$ for $\text{K}_3\text{Fe}(\text{CN})_6$. Moreover, for these values for α^2 and $e^2 Q' \langle r^{-3} \rangle$ and for $\delta/\zeta = 1/6$, Eq. (4) is found to give a good representation of both the $\Delta E_Q(T)$ curve obtained from the g -tensor and the experimental curve. This illustrates the usefulness of the distortion parameter δ .



Figs. 1–5. The quadrupole splitting ΔE_Q (in units of $e^2 Q' \langle r^{-3} \rangle$), calculated from Eq. (4), as a function of temperature (given as kT/ξ) for the various values of δ/ξ shown on the curves; the ratio β^2/α^2 is fixed at (1) 2, (2) 5/4, (3) 1, (4) 4/5, (5) 1/2

The complexes to which this theoretical treatment has so far been shown to be applicable [5, 8, 9], exhibit a temperature dependent Mössbauer quadrupole splitting. However detailed calculations for Eq. (4), plotted in Figs. 1–5, show that for most combinations of α , β and δ , the expected ΔE_Q is constant over the temperature range of interest. The compounds listed in Table 1 clearly fall into this range.

Iron (II)

Two of the compounds formally contain iron in oxidation state II, and a consideration of Mössbauer quadrupole splittings expected in strong field iron (II), 1A_1 , is therefore in order. Operating with the Hamiltonian (1) on the filled molecular orbital wavefunctions (3), yields the following temperature independent relation for the quadrupole splitting

$$\Delta E_Q = \frac{4}{7} e^2 Q' \langle r^{-3} \rangle (\beta^2 - \alpha^2). \quad (5)$$

Thus a measurable quadrupole splitting should occur only if the bonding is significantly anisotropic, and it has been observed that the quadrupole splittings are very small for a wide range of strong field iron (II) complexes [10]. Thus, starting with a formally iron (III) complex such as (8), and “feeding in” an electron to obtain an analogous iron (II) complex such as (6) or (9) would normally be expected to lead to a dramatic reduction in the Mössbauer quadrupole splitting. In fact the observed change in ΔE_Q from Table 1 is slight and in the wrong direction, and the isomer shift remains unchanged. This indicates that perhaps the central metal atom is little affected by the added electron, and may still be treated as an essentially d^5 system, a point we shall pursue further.

Compounds (1) and (2) in Table 1 have six equivalent metal-ligand bonds so that $\alpha = \beta$. Since the dithiolene ligands exert a strong crystal field, the values of $e^2 Q' \langle r^{-3} \rangle$ and α in compounds (1) and (2) may reasonably be assumed to have similar values to those of $K_3Fe(CN)_6$. In five-coordinated complexes, the screening of the iron nucleus is expected to be somewhat smaller, so that the value of $e^2 Q' \langle r^{-3} \rangle$ is expected to be greater than 8.9 mm/sec, but still appreciably smaller than the value of 12.9 mm/sec observed in high spin ferrous compounds [11]. A value of 10 mm/sec would therefore be reasonable for the five-coordinated complexes. In any case the difference between these values for $e^2 Q' \langle r^{-3} \rangle$ in the five- and six-coordinated complexes is not great compared to accuracy available from the experimental measurements, and the values of β/α and δ required to fit the results are not greatly affected. The degree of bonding with the ligands would also be expected, *a priori*, to be a little less in the five- than in the six-coordinated complexes, and hence the values of α and β should be a little greater.

If α is taken as 0.75 in compounds (1) and (2), we find that $\delta/\zeta = 1:0$ from Eq. (4). This corresponds to a splitting, 3δ of the 2T_2 state, of 1200 cm^{-1} , which indicates a considerable degree of distortion from octahedral symmetry. If, on the other hand, we treated the iron as iron (II) in compounds (1) and (2) a zero quadrupole splitting would be predicted from Eq. (5). Although the iron is formally iron (IV) in compound (2) the similarity of the Mössbauer data with compound (1) strongly suggests we may treat both compounds as iron (III).

The data for the other complexes will now be discussed in terms of Eq. (4), and the results compared with the predictions of Eq. (5). X-ray diffraction studies of the complex anions in compounds (4) [12] and (7) [13], and of the complex $[\text{CoS}_4\text{C}_4(\text{CF}_3)_4]_2$ [14], suggest that all the compounds in groups *B*, *C* and *D* in Table 1 are five-coordinated, and have a similar structure. This is further supported by chemical evidence [15]. Therefore we may take a constant value of δ/ζ for all of these compounds, and the range of β/α values will give a comparison of the effect of the various groups bonded to the fifth position. If α is taken as 0.8, we obtain $\delta/\zeta = 1.8$ (corresponding to $3\delta \doteq 2200 \text{ cm}^{-1}$) and a range of β values which are listed in Table 2, together with the observed values of ΔE_Q and those calculated from Eq. (5). The β values in groups *B* and *C* are closer to unity than in group *D*, which suggests that the bonds to the fifth position of the metal are weaker in groups *B* and *C*. This agrees well with the observation of an elongated fifth bond in a dimeric five-coordinated cobalt dithiolene [14] and with the donor properties of pyridine, which is a considerably weaker ligand than the nitrosyl group. However, the pyridine adduct (5) may have a quartet ground state [2], in which case it would not belong to the present series, so that the good agreement with expectations may be merely fortuitous. With the exception of the very low result obtained for complex (7), the β values in Table 2 are of quite reasonable magnitudes.

Table 2

Compound	δ/ζ	$e^2Q'\langle r^{-3} \rangle$	α^2	β^2	ΔE_Q Calc.		ΔE_Q Found		
					77° K	295° K	77° K	295° K	
<i>A</i> (1)	1.0	8.9	0.75	0.75	1.65	1.60	1.57	1.59	
	(2)	1.0	8.9	0.75	0.75	1.65	1.60	1.69	— ^a
<i>B</i> (3)	1.8	10	0.80	0.83	2.41	2.41	2.37	2.45	
	(4)	1.8	10	0.80	0.88	2.69	2.69	2.76	2.81
<i>C</i> (5)	1.8	10	0.80	0.84	2.45	2.45	2.41	2.51	
<i>D</i> (6)	1.8	10	0.80	0.71	1.69	1.68	1.68	1.69	
	(7)	1.8	10	0.80	0.58	0.97	0.83	0.97	— ^a
	(8)	1.8	10	0.80	0.70	1.66	1.64	1.65	1.65
	(9)	1.8	10	0.80	0.76	1.98	1.98	1.98	1.99

^a The data could not be fitted uniquely here since experimental results are available for a single temperature only.

Compounds (6) and (9) are formally iron (II) and it is interesting to examine the effect of considering these in terms of d^6 configurations. Using a value of 13 mm/sec for $e^2Q'\langle r^{-3} \rangle$, Eq. (5) reduces to

$$|\beta^2 - \alpha^2| = |\Delta E_Q|/7.4. \quad (6)$$

Thus the values of $|\beta^2 - \alpha^2|$ are 0.23 and 0.27 for complexes (6) and (9) respectively. These values would seem rather large in any complex, and are especially so when compared to the value of 0.1 (Table 2) for the isostructural iron (III) complex (8). The values 0.09 and 0.04 obtained from Eq. (4) (Table 2), and it

appears that the electronic configuration near the iron nucleus is best regarded as d^5 . On the other hand, application of Eq. (6) to the formally iron (I) complex (7) yields $|\beta^2 - \alpha^2| = 0.13$ which seems more reasonable than the larger value of 0.22 obtained from Eq. (4) (Table 2). Thus the configuration appears to be closer to d^6 than d^5 in complex (7).

The results could be explained by assuming that an electron added to a complex (such as (8)) to form an isostructural complex such as (6), goes into the d -shell (e. g. Fe (III) \rightarrow Fe (II)), and that simultaneously α and β undergo a large change, such that the quadrupole splitting remains almost unchanged. However, such a situation is hard to visualise, and seems improbable; it appears more likely that an electron, added to, or subtracted from, the complex, has a fairly small effect on the immediate configuration of the metal.

Other Contributions to the Quadrupole Splitting

A small temperature independent contribution to ΔE_Q due to the cation must be expected, but its magnitude cannot be estimated by internal comparison of the compounds in Table 1. However the contribution to ΔE_Q due to the cation is unlikely to be significant, since each of the cations is very bulky, with a single positive charge essentially located at the centre.

Whether the assumption of a common environment for the compounds in groups B–D is justified will become known when further structural data is available. However, these complexes fall into a region where the calculated ΔE_Q is not significantly affected by small variations in δ/ζ , and hence only a gross deviation from the common structure would lead to any error.

Magnetic exchange interactions occur in the dimeric compounds (3) and (4) [16, 17]. Unless the interaction is very strong, each of the unpaired electrons is essentially localised on one iron atom, and spends little time near the other iron atom. Thus each iron nucleus is affected mainly by its own d -electrons and little by those of the other iron atom. An apparent discrepancy is therefore expected between the Mössbauer spectra and the magnetic properties: while the exchange interactions impose a considerable temperature dependence upon the magnetic moment, the analogous temperature dependence of the quadrupole splitting should not be appreciable. This is observed (Table 1, 2). In monomeric complexes which have unpaired electrons localised on the ligands, similar magnetic exchange interactions are possible between these and the unpaired electron on the metal atom, but this would again have little effect on the quadrupole splitting.

Electronic Spectra

Our conclusions are in general agreement with a molecular orbital scheme [ii] (assuming C_{2v} symmetry) tentatively suggested for nitroso adducted dithiolenes by McCleverty *et al.* [3] except that complete delocalisation of the electrons is not expected. Mössbauer studies sample the electronic structure at one point only – the iron nucleus – and the indication is that the metal d -electrons are largely localised on the metal atom, while the ligand electrons are localised mainly on the ligands

(this does not hold exactly, as may be seen from the

———	a_1''	(metal d_{z^2})
———	a_2	(metal d_{xy})
———	b_1'', b_2''	(NO π^*)
———	L	(dithiolene a_2, b_1'' or b_2'')
———	a_1'	(metal $d_{x^2-y^2}$)
———	b_1', b_2'	(metal d_{xz}, d_{yz})

[ii]

values of the molecular orbital coefficients α and β in Table 2). The filling of the metal and of the ligand orbitals should therefore be at least partially independent. On this basis the scheme for complex (7), for example, would be $(b_1', b_2')^4 (a_1')^1; (L)^2 (b_1'', b_2'')^2$, or for the complex (8) (or (4), and (5)), $(b_1', b_2')^4 (a_1')^1; (L)^2$. Compound (7) has the lowest value of β in the series (Table 2), indicating the greatest degree of overlap between metal and ligand orbitals, and hence the greatest deviation from d^5 character. Thus for compound (7) a more realistic orbital scheme might be intermediate between the above and the scheme $(b_1', b_2')^4 (a_1')^2; (L)^2 (b_1'', b_2'')^1$.

Other Measurements

Unlike Mössbauer studies, magnetic susceptibility measurements sample the electronic structure (averaged) of the entire molecule. Extensive magnetic measurements over a wide temperature range are desirable, to investigate the strength of exchange interactions as well as the effects of distortion from cubic symmetry and the extent of electron delocalisation into the ligands, and at least part of this work has apparently been undertaken [18].

The room temperature magnetic moment of 1.94 B.M. [17] for complex (8) is lower than would be expected for a low spin d^5 complex, but is compatible [19] with the large distortion and considerable bonding effects indicated by the Mössbauer data. The slightly lower moment for complex (7) [17] would be expected from the very large bonding effects discussed above for this complex. These moments should be almost temperature independent, decreasing only slightly as the temperature is lowered [19]. Thus when magnetic interactions occur between two such distorted ferric ions (as in complexes (3) or (4)), the magnetism should be closely represented by the Bleaney-Bowers equation [20] (poorer agreement would be expected for interactions between species with undistorted 2T_2 ground states). Complexes (3) and (4) are analogous in this respect to dimeric cupric acetate, in which it has also been deduced that each of the two unpaired electrons is essentially localised on a separate copper atom [21]. Magnetic measurements over as wide a temperature range as possible would also give an estimate of the strength of exchange interactions between unpaired metal and ligand electrons where appropriate.

Further useful information on the electronic structures could be obtained from single crystal e.s.r. measurements where these are possible.

Conclusion

A general theory for the interpretation of Mössbauer spectra in terms of the relative bonding strengths and of the degree of distortion from octahedral

symmetry has been given previously, and the theory and a method of its application have been outlined in this paper in detail. The quadrupole splittings of the Mössbauer absorption peak in low spin iron (III) (2T_2) complexes have been calculated from the theory and given for a large range of α , β and δ values; α and β are metal-ligand molecular orbital coefficients and δ is a distortion parameter. It is found that for certain values of α , β and δ , the calculated quadrupole splitting is independent of temperature over the temperature range of interest for inorganic complexes. The quadrupole splitting in low spin iron (II) (1A_1) was also calculated and shown to be independent of δ and of temperature.

The theory has been shown to be useful for all compounds which are essentially strong-field d^5 or d^6 , even when the d -orbitals are involved in considerable molecular orbital overlap with the ligand orbitals. By way of example, some literature Mössbauer data on dithiolene complexes of iron, for which formal oxidation numbers are meaningless and magnetic susceptibility measurements give little indication of the number of d -electrons associated with the iron atom, have been interpreted in terms of the environment of the iron atom. In these complexes the quadrupole splitting is generally large and effectively independent of the temperature.

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