upon occupancy of the cavity thus appear mainly within the glycoluril moieties, not at the links between them. These alterations may represent the full extent of cucurbituril's possible response to occupancy inasmuch as the *para*-disubstituted benzene ring is at the upper limit of size that the cucurbituril cavity accommodates (Mock & Shih, 1983).

In (1) each Ca^{II} ion is coordinated to three carbonyl O atoms – two at a portal of one cage and the third at a portal of an immediate neighbor (Fig. 3). The distances are 2·358 (4) and 2·475 (4) Å [to O(5) and O(6) of one cage] and 2·468 (4) Å [to O(2′) of the other]. The perpendicular distance between the best least-squares planes of the portal O atoms of two such neighbors is 4·153 (16) Å. Octacoordination at the Ca^{II} is completed with *W*(1), *W*(2), *W*(3) and *W*(6) at 2·386 (4), 2·404 (5), 2·448 (5) and 2·713 (10) Å and O(1)[S(1)] at 2·514 (4) Å. One water of crystallization [*W*(6)] lies hydrogen-bonded 0·17 Å above the O(1)–O(6) plane and nearly equidistant from the six portal O atoms. At the center of inversion inside the cavity is found a single water molecule, a feature which recalls the encirclement of water by neutral crown compounds, first reported by Newkome, Hellen, Fronczek, DeLord, Kohli & Vogtle (1981). Thus a chain of hydrogen-bonded water molecules, *W*(6)–*W*(*I*)–*W*(6′), passes through the center of the 'empty' cage in (13).

In (1) there is also important hydrogen bonding at the portals of the cucurbituril cage. Each ammonium nitrogen, N(*X*), protrudes 0·630 (7) Å outside the plane of the six portal carbonyl O atoms and lies off-center (Fig. 2), making close approaches to O(4) and O(5) [2·822 (4) and 2·914 (4) Å], and intermediate approaches to O(3) and O(6). N(*X*) also lies significantly close to *W*(5), *W*(3) and *W*(6) [distances are 2·856 (6), 2·869 (6) and 3·10 (3) Å].

Part of this work was performed while on sabbatical leave at the University of New Mexico. The author thanks Professor Robert Tapscott and Eileen Duesler for their hospitality and assistance.

References

BLESSING, R. H. & DETITTA, G. T. (1984). *Acta Cryst.* Submitted.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–108.

FREEMAN, W. A., MOCK, W. L. & SHIH, N.-Y. (1981). *J. Am. Chem. Soc.* **103**, 7367–7368.

MAIN, P., WOOLFSON, M. M., LESSINGER, L. & GERMAIN, G. (1976). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOCK, W. L., IRRA, T. A., WEPSIEC, J. P. & MANIMARAN, T. L. (1983). *J. Org. Chem.* **48**, 3619–3620.

MOCK, W. L. & SHIH, N.-Y. (1983). *J. Org. Chem.* **48**, 3618–3619.

MORAN, J. R., KARBACH, S. & CRAM, D. J. (1982). *J. Am. Chem. Soc.* **104**, 5826–5828.

NEWKOME, G. R., HELLEN, C. R. T., FRONCZEK, F. R., DELORD, T. J., KOHLI, D. K. & VOGTLE, F. (1981). *J. Am. Chem. Soc.* **103**, 7376–7378.

SHELDRICK, G. M. (1981). *Nicolet SHELXTL Operations Manual.* Nicolet XRD Corp., Cupertino, CA.

SHIH, N.-Y. (1981). *Host–Guest Chemistry of Cucurbituril.* Doctoral Dissertation, Univ. of Illinois at Chicago.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

VAN ETTEN, R. L., SEBASTIAN, J. F., CLOWES, G. A. & BENDER, M. L. (1967). *J. Am. Chem. Soc.* **89**, 3242–3253.

Acta Cryst. (1984). B**40**, 387–397

Dynamic Processes in Crystals Examined Through Difference Vibrational Parameters ΔU: The Low-Spin–High-Spin Transition in Tris(dithiocarbamato)iron(III) Complexes

BY K. CHANDRASEKHAR AND H. B. BÜRGI

Laboratorium für Chemische und Mineralogische Kristallographie der Universität, CH-3012 Bern, Switzerland

(*Received* 25 *July* 1983; *accepted* 5 *December* 1983)

Abstract

Difference vibrational parameters $\Delta U(z)$ evaluated along internuclear directions between bonded atoms contain physical information on internal molecular motion. For a number of metal complexes, showing small-amplitude motion, ΔU's from diffraction experiments are found to be in good agreement with ΔU's calculated from vibrational force fields. Typical values are in the range 0·002–0·003 Å^2. For molecules showing large-amplitude deformations of bond length, experimental ΔU's agree with those calculated from simple models. As an example, data for tris(dithiocarbamato)iron(III) complexes [$(R_2NCS_2)_3Fe^{III}$], taken from the literature, are analysed in detail. This class of compounds shows a spin equilibrium in the solid state which depends on temperature, on the substituents attached to the dithiocarbamate skeleton, and on solvate molecules, if any. The Fe–S bond distance varies between ~2·30 Å in the low-spin state and ~2·45 Å in the high-spin state, the exact value depending on the

0108-7681/84/040387-11$01.50

population of each spin state. ΔU's observed for a sample of 35 molecules vary as a quadratic function of the observed Fe–S distances (correlation coefficient ~0·80). The correlation may be understood in terms of a distribution of the ligands and in particular of the S atoms over two positions which are about 0·15 Å apart. This leads to an apparent increase of the vibrational amplitude of S approximately in the direction of the Fe–S bond, the magnitude of this increase depending on the population of the spin states. The insensitivity of ΔU's to various systematic errors in the diffraction data and their sensitivity to the model of the electron density function are discussed. The use of difference vibrational parameters to study problems of compositional and positional disorder (*e.g.* Al/Si) is suggested. Systematic analyses of the type presented here would be more efficient if **U**'s were available on a data base, or even if authors of papers would take greater care in reporting them.

Introduction

In many examples of structure determination by diffraction methods the parameters associated with individual atomic vibrational motion tensors seem to be a convenient vehicle to minimize the discrepancy between observed and calculated structure factors; the physical significance of these tensors is not always clear and the long lists of tensor components are quite often a nuisance to authors of papers and to their publishers as well. This has led to shadowy existence of **U**'s, **B**'s or $\boldsymbol{\beta}$'s in forlorn corners of crystallographers' writing tables, on dusty magnetic tapes or in other depositories. Procuring these parameters often entails considerable effort and patience, and, as a consequence, the ability to assess the qualitative and quantitative information contained in them seems to be a rare skill.

In this paper a particular aspect of vibrational parameters is analysed systematically. In particular, tris(dithiocarbamato)iron(III) complexes are studied because they show a high-spin–low-spin equilibrium (Fig. 1) in the solid state (Cambi & Szegö, 1931, 1933; White, Roper, Kokot, Waterman & Martin, 1964; Ewald, Martin, Ross & White, 1964). As will be discussed below this process involves changes in Fe–S bond lengths and affects the **U**'s in a systematic manner. The changes can be modelled from simple theoretical calculations. A comparison of theoretical and experimental vibrational parameters indicates which type of physical information can be extracted routinely from the **U**'s of present-day diffraction experiments.

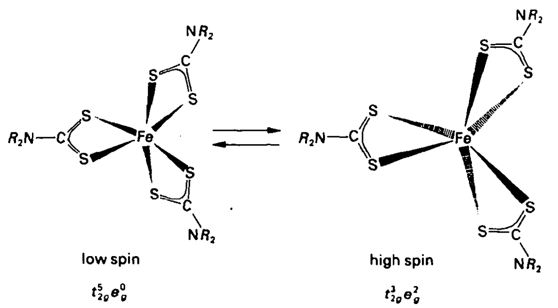

Fig. 1. High-spin–low-spin equilibrium in tris(dithiocarbamato)-iron(III) complexes. Note the variation in Fe–S bond lengths (exaggerated).

Background

Attempts to interpret **U**'s in terms of coupled motion of atoms fall into three categories.

(1) The lattice dynamical approach. The **U**'s are calculated as a sum of contributions, one from each of the normal modes of the crystal. A prerequisite for this approach is the availability of a theoretical or experimental force field (for recent reviews see Willis & Pryor, 1975; Willis, 1982; Bürgi, 1982; Gramaccioli, Filippini & Simonetta, 1982). The criterion for a successful interpretation is agreement between observed **U**'s and those calculated from the force field.

(2) Interpretations of the anisotropies in the observed **U**'s. The best known method in this class is rigid-body analysis introduced by Cruickshank (1956), generalized by Schomaker & Trueblood (1968) and modified to take into account certain types of intramolecular motions by Johnson (1970*a*) and Dunitz & White (1973). The method and its variants are based on assumptions about the relative phases of atomic motions. A successful rigid- or semi-rigid-body analysis requires that the observed **U**'s be expressible to within experimental accuracy by a limited number of model parameters such as **T**, **L** and **S** tensor elements. Sometimes these parameters can be compared with those obtained independently from other techniques (for recent references see Trueblood & Dunitz, 1983; Gavezzotti & Simonetta, 1982; Bonadeo & Burgos, 1982).

(3) Interpretation of differences between observed **U**'s of different atoms. The best known model in this class is that involving riding motion of an atom *B*, usually a light atom, on an atom *A*, usually a heavy one (Busing & Levy, 1964; for related models see Johnson, 1970*b*). In this model the magnitudes of **U** in two directions perpendicular to the bond *A–B* are evaluated $[U(x), U(y)]$. The differences $\Delta U(x) = U_B(x) - U_A(x)$, $\Delta U(y) = U_B(y) - U_A(y)$ are measures of the amplitudes of the riding motion. The validity of assuming riding motion is usually judged on the basis of the ensuing correction in bond lengths or in rare cases from spectroscopic data.

As far as the magnitudes of **U** along the *A–B* bond direction $[U(z)]$ are concerned, Harel & Hirshfeld (1975) postulated $U_B(z) - U_A(z) = 0$ for covalently bonded atoms at least as heavy as carbon; this postulate was shown to hold within ~0·001 Å^2 if applied to organic compounds (Hirshfeld, 1976). A more detailed discussion of the postulate is given below.

Hirshfeld's rigid-bond postulate

For molecular crystals the postulate may be given in terms of contributions from inter- and intramolecular vibrations as

$$\Delta U(z) = U_B(z, \text{inter}) - U_A(z, \text{inter}) + \sum_{i=1}^{3N-6} [U_B^i(z, \text{intra}) - U_A^i(z, \text{intra})] = 0.$$

Under certain conditions the two types of contributions are uncorrelated (Scheringer & Fadini, 1979) and may hence be treated separately. If the $U(z, \text{inter})$ alone are considered [$U(z, \text{intra}) = 0$] the molecule by definition behaves like a rigid body in which the atoms have no relative motion, *i.e.* the first two terms evaluated between a pair of atoms in the same molecule cancel each other. Usually the $U(z, \text{intra})$ cannot be neglected and it is not easy to see that the intramolecular contributions should also add up to zero nor is it easy to estimate the order of magnitude of the difference if they do not. Indeed the sum of the differences of the intramolecular contributions depends critically on the masses of the atoms A and B, on the type of bond between them, on their environment and on the temperature of the experiment. This is best shown by a few examples for which the components $U^i(z, \text{intra})$ may be calculated from force constants determined through vibrational spectroscopy (see Willis & Pryor, 1975; Scheringer & Fadini, 1979) or from other information that is independent of the U's from diffraction experiments.

(1) CO_2. With the force constants from Herzberg (1945) the difference $\Delta U(z)$ at 300 K is 0·000021 Å^2, too small to be measured by even the most accurate of today's diffraction experiments. Thus triatomic carbon dioxide with its C=O double bond follows Hirshfeld's postulate extremely well.

(2) $Ni^{II}(NH_3)_6$. With the force field of Cyvin, Cyvin, Schmidt, Müller & Brunvoll (1976), who considered NH_3 as a point mass, $\Delta U(z)$ for the Ni–N bonds is calculated to be 0·0030 Å^2 (at 300 K), about two orders of magnitude larger than for CO_2. Observed values of $\Delta U(z)$ for various complexes $Ni^{II}(L_n)_m$ (L_n: n-dentate aliphatic or aromatic amine, NO_2^-; $m.n = 6$) are in the range 0·0020–0·0027 Å^2 with an outlier at 0·0094 Å^2 (Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979).

(3) $Ru^{II}(H_2O)_6$. The force field of Bernhard & Ludi (1984) yields $\Delta U(z) = 0{\cdot}0022$ Å^2 (at 300 K); the experimental value obtained by averaging over the three independent observations in triclinic $[Ru(H_2O)_6]^{2+}(CH_3C_6H_4SO_3)_2^-$ is 0·0020 (7) Å^2 (Bernhard, Bürgi, Hauser, Lehmann & Ludi, 1982). The order of magnitude of $\Delta U(z)$ in this and the previous example is typical for transition-metal complexes with first-row ligand atoms and can just about be verified from routine diffraction experiments of today.

(4) Examples involving large-amplitude motion. Dynamic Jahn–Teller distortion of octahedrally coordinated Cu^{II} involves large-amplitude displacements of six chemically equivalent, peripheral ligands but not of the central metal atom (Fig. 2). The contribution to $\Delta U(z)$ arising from the large-amplitude motion has been calculated to be ~0·017 Å^2 which is an order of magnitude larger than the values given above for $Ni^{II}(NH_3)_6$ or $Ru^{II}(H_2O)_6$. Such an effect can be seen clearly and consistently even from diffraction experiments of only moderate accuracy: the observed values of $\Delta U(z)$ are about 0·020 Å^2. They are slightly larger than the calculated ones because they are composed of two contributions: one from the large-amplitude stretching motion (Fig. 2) and another from the five remaining small-amplitude stretching motions. The latter is comparable in magnitude to $\Delta U(z)$ observed or calculated for hexaammine nickel(II) complexes (~0·003 Å^2). Analogous observations have been reported for $Mn^{III}F_6^-$ complexes (Vedani, 1981). Details are discussed extensively elsewhere (Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979).

This paper is concerned with the low-spin–high-spin (l.s.–h.s.) equilibrium in tris(dithiocarbamato)iron(III) complexes, $[(R_2NCS_2)_3Fe^{III}]$. The nature of the transition has been examined for various dithiocarbamate ligands, with and without solvate molecules in the crystal structures and at various temperatures for a total of 35 cases (Table 1). In the $t_{2g}^5e_g^0$ electronic configuration Fe^{III} shows low-spin behaviour; there are no antibonding σ electrons and the Fe-S distances are therefore ~0·15 Å shorter than in the $t_{2g}^3e_g^2$ configuration with two antibonding σ electrons and high-spin behaviour. The breathing motion involved in the l.s.–h.s. transition (Fig. 1) is expected to manifest itself in $\Delta U(z)$. A number of tris(dithiocarbamato)–transition-metal complexes that do not show a spin equilibrium have been included in our study for purposes of comparison (Table 2).

Data retrieval and organization

Molecules of the type $[(XCS_2)_3M]$, where X is RO, R_2N, R_2C and M is Cr^{III}, Fe^{III}, Fe^{IV}, Co^{III}, Ni^{II},

Fig. 2. Dynamic Jahn–Teller distortion in octahedral Cu^{II} complexes with six chemically equivalent ligands showing coupling of ligand displacements. For amines or nitrite anions as ligands the Cu–N bond lengths oscillate between ~2·05 and ~2·35 Å.

Table 1. *Parameters relating to data collection, structure refinement and spin state for* $[(XCS_2)_3Fe^{III}]$ *complexes*

(*a*)	T(K) (*b*)	μ_{eff} (BM)	Radiation	d_{min} (Å) (*c*)	μ (cm^{-1})	Scattering factors f (*d*)	Scattering factors f', f'' (*e*)	R (*f*)	R_w (*f*)	S (*f*)
(1) $Fe[S_2CN(CH_3)_2]_3$	25 (3)	1·80	Cu, Mo	1·09 0·50	135·2 15·2	?	?	0·046	0·061	1·098
(2) $Fe[S_2CN(CH_3)_2]_3$	150	2·4	Mo	0·84	14·3	?	No	0·058	0·069	1·9
(3) $Fe[S_2CN(CH_3)_2]_3$	295	4·1	Cu	0·82	128·4	?	No	0·067	0·079	1·6
(4) $Fe[S_2CN(CH_3)_2]_3$	400 (1)	4·83	Cu	0·82	125·1	?	?	0·058	0·065	1·070
(5) $Fe[S_2CN(CH_2)_4]_3.0{\cdot}5CH_2Cl_2$	297 (1)	2·19	Mo	0·93	13·1	*N*	Fe, S	0·055	0·042	1·447
(6) $Fe[S_2CN(CH_2)_4]_3$; PhI	RT	5·9	Cu	*F*	98	*N*	Fe	0·13	0·18	—
(7) $Fe[S_2CN(CH_2)_4]_3$; PhII	295 (1)	5·9	Mo	0·71	12·6	*N*	?	0·059	0·069	—
(8) $Fe[S_2CN(CH_2)_4]_3.0{\cdot}5C_6H_6$	150	5·8	Mo	0·87	11·2	—	—	0·051	0·050	2·7
(9) $Fe[S_2CN(CH_2)_4]_3.0{\cdot}5C_6H_6$; DtII	295	5·9	Mo	0·87	11.2	—	—	0·042	0·035	1·9
(10) $Fe[S_2CN(CH_2)_4]_3.0{\cdot}5C_6H_6$; DtI	292	5·9	Mo	0·81	11·2	?	?	0·045	0·048	2·01
(11) $Fe[S_2CN(C_2H_5)_2]_3$	79 (1)	2·2	Mo	0·71	11·6	—	—	0·068	0·083	—
(12) $Fe[S_2CN(C_2H_5)_2]_3$	297	4·24	Mo	0·93	11·6	—	—	0·054	0·061	—
(13) $Fe[S_2CN(CH_2)_4O]_3.H_2O$	292	5·6	Mo	0·87	11·4	?	Fe, S	0·039	0·049	2·19
(14) $Fe[S_2CN(CH_2)_4O]_3.CH_2Cl_2$; PhII	20	3·80	Mo	1·04	13·1	?	?	0·055	0·067	2·35
(15) $Fe[S_2CN(CH_2)_4O]_3.CH_2Cl_2$; PhII	110	4·45	Mo	0·84	13·0	?	?	0·062	0·086	1·29
(16) $Fe[S_2CN(CH_2)_4O]_3.CH_2Cl_2$; PhI	178	5·05	Mo	0·84	12·7	?	?	0·061	0·083	3·53
(17) $Fe[S_2CN(CH_2)_4O]_3.CH_2Cl_2$; PhI, DtII	293	5·60	Mo	0·84	12·4	?	?	0·041	0·054	2·07
(18) $Fe[S_2CN(CH_2)_4O]_3.CH_2Cl_2$; PhI, DtI	298	5·1(*g*)	Mo	0·93	12·6	*N*	?	0·063	0·061	—
(19) $Fe[S_2CN(CH_2)_4O]_3.CH_2Cl_2$; PhIII	293	5·92	Mo	0·84	13·4	?	?	0·028	0·034	0·47
(20) $Fe[S_2CN(CH_2)_4O]_3.CHCl_3$	292	5·45	Mo	0·87	12·9(*h*)	?	Fe, S	0·040	0·047	1·95
(21) $Fe[S_2CN(CH_2)_4O]_3.C_6H_5NO_2$	292	4·00	Mo	0·87	9·9	?	Fe, S	0·035	0·036	1·57
(22) $Fe[S_2CN(CH_2)_4O]_3.2C_6H_6$	292	3·50	Mo	0·81	8·5	?	?	0·047	0·061	4·10
(23) $Fe[S_2CN(C_2H_4OH)_2]_3$	150	2·40	Mo	0·84	11·0	?	—	0·078	0·112	1·86
(24) $Fe[S_2CN(C_2H_4OH)_2]_3$	295	4·20	Mo	0·84	10·8	?	—	0·067	0·095	1·76
(25) $Fe[S_2CNCH_3C_6H_5]_3$	RT	3·0	Cu	*F*	86	*N*	Fe	0·087	0·121	—
(26) $Fe[S_2CH(C_3H_4N)_2]_3.0{\cdot}5CHCl_3$	210	3·19	Mo	0·83	10·4	?	?	0·048	0·068	0·938
(27) $Fe[S_2CN(C_3H_4N)_2]_3.0{\cdot}5CHCl_3$	297	3·94	Mo	0·83	10·2	?	?	0·061	0·080	1·015
(28) $Fe[S_2CN(C_4H_9)_2]_3$	RT	5·32	Co	*F*	56·1(*i*)	—	—	0·075	—	1·98
(29) $Fe[S_2CN(C_4H_9)_2]_3.C_6H_6$	295 (1)	3·6	Mo	0·84	6·8	*N*	Fe, S	0·071	0·098	—
(30) $Fe[S_2CN(CH_2C_6H_5)_2]_3$	150	2·47	Mo	1·04	6·8	?	?	0·063	0·068	1·70
(31) $Fe[S_2CN(CH_2C_6H_5)_2]_3$	295	3·45	Mo	0·91	6·6	?	?	0·063	0·073	1·62
(32) $Fe[S_2COC_2H_5]_3$	RT	2·72	Fe	1·03	149·7	—	—	0·077	—	—
(33) $Fe[S_2CSC_4H_9]_3$	295	2·5	Cu	1·02	117	*N*	?	0·060	0·085	—

Notes: (*a*) Dt: determination, Ph: phase; *U* of C, N atoms isotropic in Nos. (6), (25) and (30), anisotropic in the rest. (*b*) RT: 'room temperature' specified by author; uncertainty in temperature indicated where available. (*c*) *F*: film data. (*d*) ?: charge of Fe, S not specified; *N*: neutral atoms; —: no information on fs. (*e*) ?: author states 'anomalous-dispersion corrections applied' or similar, unclear whether f' or f'' or both; No: anomalous-dispersion corrections not applied; Fe, S: f', f'' applied for Fe, S; Fe: f', f'' applied for Fe; –: no information on f', f''. (*f*) $R = \sum \| |F_o| - |F_c| \| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$; $S = [\sum w(|F_o| - |F_c|)^2/(NO-NV)]^{1/2}$, NO = number of observations, NV = number of variables; –: no information. (*g*) Value of μ_{eff} quoted appears to be in error, perhaps taken from another temperature. (*h*) Absorption correction not applied. (*i*) No information on absorption correction.

Table 2. *Parameters relating to data collection, structure refinement and spin state for* $[(XCS_2)_3M]$ *complexes* $(M \neq Fe^{III})$

For notes (*a*)–(*i*) see Table 1.

(*a*)	T(K) (*b*)	Spin state	Radiation	d_{min} (Å) (*c*)	μ (cm^{-1})	Scattering factors f (*d*)	Scattering factors f', f'' (*e*)	R (*f*)	R_w (*f*)	S (*f*)
(34) $Cr[S_2CN(CH_2)_4)O]_3.CH_2Cl_2$	—	$t_{2g}^3 e_g^0$	Mo	0·87	11·3(*h*)	?	?	0·043	0·048	1·35
(35) $Cr[S_2CN(CH_2)_4O]_3.2C_6H_6$	292	$t_{2g}^3 e_g^0$	Mo	0·81	7·3(*h*)	?	?	0·032	0·029	0·81
(36) $Fe[S_2CC(COOC_2H_5)_2]_3[PC_7H_7(C_6H_5)_3]_2$	—	$t_{2g}^4 e_g^0$	Mo	1·04	5·0(*i*)	*N*	Fe, S	0·042	0·051	1·50
(37) $Co[S_2CN(C_2H_5)_2]_3$; DtI	—	$t_{2g}^6 e_g^0$	Mo	*F*	12·9	?	—	0·062	0·074	—
(38) $Co[S_2CN(C_2H_5)_2]_3$; DtII	—	$t_{2g}^6 e_g^0$	Mo	*F*	12·9(*h*)	—	—	0·064	—	—
(39) $Ni[S_2CN(C_4H_9)_2]_3Br$	—	$t_{2g}^6 e_g^0$	Cu	0·84	51·1	Ni^+, S^0 Br^-	Ni, S Br	0·038	0·048	0·89
(40) $Ni[S_2COCH_2CH(CH_3)_2]_3[N(CH_3)_4]$	—	$t_{2g}^6 e_g^2$	Mo	1·04	10·8(*h*)	?	?	0·050	0·041	—
(41) $Ni[S_2COC_6H_{11}]_3[N(CH_3)_4].(CH_3)_2CO$	—	$t_{2g}^6 e_g^2$	Mo	1·04	8·8(*h*)	?	?	0·060	0·051	—
(42) $Ga[S_2CN(C_2H_5)_2]_3$	—	$t_{2g}^6 e_g^4$	Cu	1·01	63·4	*N*	Ga, S	0·034	0·053	—

Ni^{IV}, Ga^{III}, were retrieved from the Cambridge Structural Database (CSD; Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979), version of October 1982. For Fe^{III} complexes 23 studies at various temperatures encompassing 17 different molecules were found; subsequently 3 studies (for 2 different molecules) were located in the literature and unpublished results from 7 recent studies (for 2 different molecules) were obtained through private communications. Coordinate data were generally available in the literature but anisotropic thermal parameters for about half of the studies had to be obtained from depositories or individuals. For non-Fe^{III} complexes the analysis has been restricted to nine studies involving only first-row transition-metal ions and for which anisotropic thermal parameters were either available in the literature or could be procured easily from the British Library Lending Division. The bibliography is listed in Table 6.

Various parameters pertaining to data collection and structure refinement are compiled in Tables 1 and 2 to make possible a critical assessment of the data on which our study is based. The unweighted R covers a broad range from 0·029 to 0·13 with 16 values $\leq 0{\cdot}050$, 24 between 0·050 and 0·080 and 2, both from film data, $>0{\cdot}080$. Reported errors in observations of unit weight range from 0·47 to 4·1. Mo $K\alpha$ radiation was used in most cases, Cu $K\alpha$, Co $K\alpha$ and Fe $K\alpha$ radiation in the remaining few. Absorption coefficients μ are in the range 5·0 to 149·7 cm^{-1} and absorption corrections were applied in all cases except six and this is clearly stated in the papers. For entries (28) in Table 1 and (36) in Table 2 no information on absorption correction is given. There is considerable ambiguity in the authors' statements regarding scattering factors and anomalous-dispersion corrections used in the structure refinement. In only 10 cases were atomic charges specified unambiguously: in 25 cases the authors loosely refer to 'atomic scattering factors', an expression which is used for both neutral and charged atomic species in *International Tables for X-ray Crystallography* (1974); in the remaining 7 cases there is no mention of the source and nature of the scattering factors. In 12 cases it is clearly stated which components, if any, of anomalous-dispersion corrections have been applied and to which atoms; in 20 cases it is stated that 'anomalous-dispersion corrections were applied' or similarly; in the remaining 10 cases no information is given. In summary, we feel that the presentation of such detail more often than not leaves something to be desired.

A total of over 6000 anisotropic vibrational parameters and corresponding e.s.d.'s had to be laboriously typed on a computer terminal for calculation of ΔU's and their e.s.d.'s. All sorts of shortcomings in the reported vibrational parameters were encountered; they are similar to those described by Trueblood & Dunitz (1983): for entry (18) there was no indication of the form of the anisotropic temperature factor and the β's of C, N and O were ten times smaller and twice as accurate as those of Fe, S (and Cl). It is practically certain that for C, N and O the multiplicative factor is in error (10^4 instead of 10^3). For entry (22) all vibrational parameters are very likely too large by a factor of 10 and we have corrected them to obtain physically reasonable quantities. The temperature-factor expression for entry (7) is given in an unconventional form; it assumes an implicit factor of 2 for the off-diagonal U_{ij}'s leading to $\langle \Delta U(\text{Fe–S})\rangle = 0{\cdot}0071$ Å^2. Using the reported U_{ij}'s with the conventional form showing an explicit factor of 2 leads to $\langle \Delta U(\text{Fe–S})\rangle = 0{\cdot}0031$ Å^2, in much better agreement with the general trend described later for the other compounds. Besides, thermal parameters are presented in various formats. Consequently, data input and subsequent re-checking involves considerable time and effort. Finally it seems to be the policy of certain depositories to despatch requested thermal parameters by surface mail (taking three months to arrive at the destination!) and there are authors who either do not respond to requests at all or are forced by circumstances to do so only after a very considerable lapse of time. It should be mentioned, however, that information pertaining to articles in *Acta Crystallographica* is usually obtained in a matter of a few weeks.

It is clear from the above that for efficient analyses of the type reported here a database containing coordinates as well as anisotropic vibrational parameters is imperative. The Inorganic Crystal Structure Database (ICSD; Bergerhoff, Hundt & Sievers, 1982) recently made available represents a first step in this direction. A critical annotation of the vibrational parameters as is done for the atomic coordinates in the CSD would be desirable.

The program *THMB* (Trueblood, 1982) was used to evaluate M–S, S–C, C–X and S···S distances as well as ΔU's along the first three bonds. Average values of bond distances and ΔU's were calculated assuming D_3 symmetry and are presented in Tables 3 and 4. For the M–S bond length and its ΔU averaged experimental errors, $\langle\sigma\rangle$, and root-mean-square deviations from the mean, σ', are also given. In passing we note that some of our calculated Fe–S distances differ from the published values by as much as 0·008 Å [entries (5) and (10)].

Results: vibrational amplitudes

Some of the results given in Table 3 are shown as a scatterplot in Fig. 3. For all molecules except one the $\langle \Delta U\rangle$'s along the Fe–S bond are positive, between 0·0010 and 0·0096 Å^2. Of the 35 values only 18 show

Table 3. *Distances and difference vibrational parameters along bond directions calculated from X-ray structure data on* Fe$^{\mathrm{III}}$ *complexes*

$\langle d\rangle$ is the average distance $X-Y$ in Å, $\langle\Delta U\rangle$ the average of $\Delta U=U(Y)-U(X)$ along the bonds $X-Y$ in Å$^2\times10^4$, $\langle\sigma(d)\rangle$ the average e.s.d. in d, $\langle\sigma(\Delta U)\rangle=\langle\{\sigma^2[U(X)]+\sigma^2[U(Y)]\}^{1/2}\rangle$ evaluated along the $X-Y$ bond, $\sigma'(d)$ and $\sigma'(\Delta U)$ the r.m.s. deviations from the respective means.

Space group	Site symmetry	Fe–S bond						S–C bond (*a*)		C–N bond (*b*)		Bite (*c*)
		$\langle d\rangle$	$\langle\sigma(d)\rangle$	$\sigma'(d)$	$\langle\Delta U\rangle$	$\langle\sigma(\Delta U)\rangle$	$\sigma'(\Delta U)$	$\langle d\rangle$	$\langle\Delta U\rangle$	$\langle d\rangle$	$\langle\Delta U\rangle$	$\langle d(\mathrm{S}\ldots\mathrm{S})\rangle$
(1) *Pbca*	1	2·303	0·004	0·008	39	13	17	1·719	12	1·315	−71	2·827
(2) *Pbca*	1	2·339	0·002	0·008	52	13	19	1·713	40	1·321	−12	2·843
(3) *Pbca*	1	2·396	0·002	0·012	−19	13	25	1·713	34	1·316	−6	2·872
(4) *Pbca*	1	2·415	0·003	0·010	52	24	20	1·709	69	1·304	28	2·878
(5) $P2_1/c$	1	2·301	0·001	0·013	19	8	10	1·688	45	1·368	−48	2·818
(6) $P2_1/n$	1	2·406	0·010	0·021	65	61	35	1·703	—	1·310	—	2·911
(7) $P2_1/a$	1	2·456	0·002	0·020	31	7	12	1·720	31	1·312	−30	2·910
(8) $P2_1/n$	1	2·427	0·001	0·013	58	11	33	1·722	25	1·308	−27	2·911
(9) $P2_1/n$	1	2·435	0·001	0·010	54	9	34	1·712	48	1·320	−56	2·906
(10) $P2_1/n$	1	2·439	0·001	0·010	40	10	31	1·717	35	1·321	−27	2·911
(11) $C2/n$	2	2·307	0·001	0·005	11	7	9	1·720	12	1·333	−32	2·837
(12) $P2_1/c$	1	2·357	0·003	0·005	54	20	19	1·709	−5	1·337	43	2·845
(13) $P\bar{1}$	1	2·443	0·001	0·010	39	7	14	1·721	37	1·318	−63	2·895
(14) $P\bar{1}$	1	2·357	0·005	0·007	91	27	118	1·714	−17	1·327	114	2·843
(15) $P\bar{1}$	1	2·372	0·002	0·009	86	14	137	1·721	34	1·319	−81	2·854
(16) $P\bar{1}$	1	2·401	0·003	0·010	65	18	33	1·719	70	1·325	−77	2·869
(17) $P\bar{1}$	1	2·427	0·003	0·010	50	16	46	1·715	59	1·321	−48	2·878
(18) $P\bar{1}$	1	2·430	0·004	0·011	53	28	47	1·719	−36	1·314	−31	2·880
(19) $P\bar{1}$	1	2·441	0·001	0·009	35	6	12	1·718	43	1·322	−49	2·892
(20) $P\bar{1}$	1	2·416	0·001	0·012	57	8	11	1·719	28	1·324	−20	2·884
(21) $P2_1/c$	1	2·354	0·001	0·013	65	6	43	1·716	31	1·325	−52	2·849
(22) $C2/c$	2	2·317	0·001	0·006	31	3	6	1·715	23	1·318	−17	2·837
(23) $P\bar{1}$	1	2·331	0·003	0·007	66	17	14	1·725	17	1·318	−18	2·840
(24) $P\bar{1}$	1	2·390	0·003	0·007	96	17	15	1·723	11	1·320	24	2·867
(25) $P2_1/a$	1	2·312	0·009	0·019	21	59	90	1·687	—	1·380	—	2·819
(26) $P\bar{1}$	1	2·308	0·002	0·008	25	9	18	1·712	47	1·342	−5	2·831
(27) $P\bar{1}$	1	2·324	0·002	0·008	51	10	29	1·714	37	1·324	6	2·838
(28) $C2/c$	2	2·417	0·003	0·005	71	26(*d*)	13	1·703	38	1·341	−4	2·865
(29) *Pncn*	2	2·341	0·002	0·004	62	22	9	1·711	11	1·332	35	2·837
(30) $P2_1$	1	2·314	0·007	0·014	35	56	28	1·706	—	1·328	—	2·827
	1	2·306	0·007	0·016	10	53	49	1·706	—	1·341	—	2·839
(31) $P2_1$	1	2·349	0·005	0·021	60	42	59	1·715	73	1·315	7	2·848
	1	2·327	0·005	0·014	63	40	43	1·709	127	1·329	46	2·840
(32) $R\bar{3}$	3	2·317	0·003	0·012	31	17(*e*)	5	1·688	13	—	—	2·836
(33) $P\bar{1}$	1	2·297	0·003	0·007	19	16	14	1·695	42	—	—	2·801

Notes: (*a*) $0{\cdot}001\le\langle\sigma(d)\rangle\le0{\cdot}030$; $0{\cdot}001\le\sigma'(d)\le0{\cdot}049$; $12\le\langle\sigma(\Delta U)\rangle\le130$; $6\le\sigma'(\Delta U)\le276$; $|\langle\Delta U\rangle|\le1.5\langle\sigma(\Delta U)\rangle$. (*b*) $0{\cdot}003\le\langle\sigma(d)\rangle\le0{\cdot}033$; $0{\cdot}003\le\sigma'(d)\le0{\cdot}059$; $18\le\langle\sigma(\Delta U)\rangle\le154$; $6\le\sigma'(\Delta U)\le358$; $|\langle\Delta U\rangle|\le2.1\langle\sigma(\Delta U)\rangle$. (*c*) $0{\cdot}001\le\langle\sigma(d)\rangle\le0{\cdot}010$; $0{\cdot}001\le\sigma'(d)\le0{\cdot}017$. (*d*) $\langle\sigma(\Delta U)\rangle$ estimated from $\sigma(U)$ of C. (*e*) $\langle\sigma(\Delta U)\rangle$ estimated as the average of $\langle\sigma(\Delta U)\rangle$'s in structure determinations of comparable *R* value.

$\langle\Delta U\rangle\ge3\langle\sigma(\Delta U)\rangle$, and only 7 show $\langle\Delta U\rangle\ge3\sigma'(\Delta U)$. In spite of the scant significance of individual $\langle\Delta U\rangle$'s the data as a whole show a nonlinear dependence of $\langle\Delta U\rangle$ on $\langle d\rangle$.

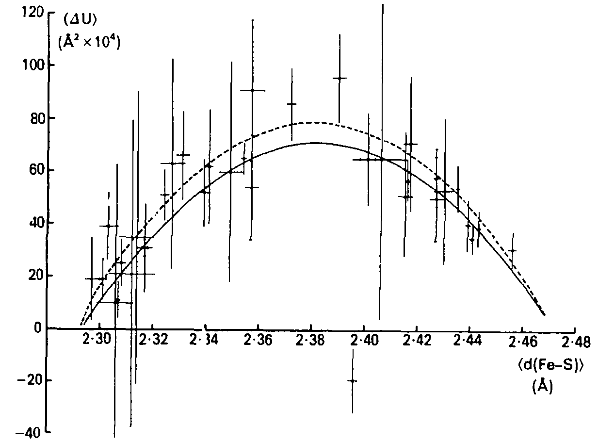

Fig. 3. Scatterplot of $\langle\Delta U(\mathrm{Fe{-}S})\rangle$ *vs* $\langle d(\mathrm{Fe{-}S})\rangle$. Error bars are $\langle\sigma\rangle$ from Table 3. $\langle\Delta U\rangle$ implies $\langle\Delta U(z)\rangle$. The dotted curve is based on the model $\Delta U=0{\cdot}0078+0{\cdot}0120\delta-0{\cdot}93\delta^2$, the solid curve on the weighted regression $\langle\Delta U\rangle=0{\cdot}0071+0{\cdot}136\delta-0{\cdot}88\delta^2$ (see text).

Table 4. *Distances and difference vibrational parameters along bond directions calculated from X-ray structure data on non-*Fe$^{\mathrm{III}}$ *complexes*

Definitions of quantities are as indicated for Table 3.

Space group	Site symmetry	*M*–S bond					
		$\langle d\rangle$	$\langle\sigma(d)\rangle$	$\sigma'(d)$	$\langle\Delta U\rangle$	$\langle\sigma(\Delta U)\rangle$	$\sigma'(\Delta U)$
(34) $P\bar{1}$	1	2·406	0·003	0·012	20	15	28
(35) $C2/c$	2	2·396	0·003	0·010	10	15	6
(36) $C2/c$	2	2·298	0·002	0·009	9	12	18
(37) $C2/c$	2	2·258	0·003	0·003	61	20	42
(38) $C2/c$	2	2·261	0·003	0·011	13	17	11
(39) $P\bar{3}1c$	32	2·261	0·001	—	13	13	—
(40) $P2_1/c$	1	2·433	0·002	0·035	38	21	24
(41) Cc	1	2·428	0·005	0·029	35	42	121
(42) $A2/a$	2	2·437	0·002	0·029	34	11	17

The points at the lower end of the distribution with $\langle d\rangle\sim2{\cdot}30$ Å, $\langle\Delta U\rangle\sim0{\cdot}0010$ Å^2 are obtained from molecules with $t_{2g}^5e_g^0$ electronic configuration whose magnetic moments are typical for low-spin behaviour ($\mu_{\mathrm{eff}}\sim2{\cdot}5$ BM, $1\ \mathrm{BM}\equiv9{\cdot}27\times10^{-24}\ \mathrm{A\,m^2}$). Their $\langle\Delta U\rangle$'s may be compared to those of dithiocarbamate complexes in low-spin $t_{2g}^ne_g^0$ electronic configurations

($n = 3, 4, 6$; Table 4). A weighted average of the first six entries in Table 4 yields $\langle \Delta U\rangle = 0{\cdot}0017\,(16)$ Å^2, in good agreement with the values for the low-spin Fe complexes. The points at the upper end of the distribution with $\langle d\rangle \sim 2{\cdot}45$ Å, $\langle \Delta U\rangle \sim 0{\cdot}0030$ Å^2 refer to molecules with $t_{2g}^3 e_g^2$ electronic configuration showing high-spin behaviour ($\mu_{\rm eff} \sim 5{\cdot}8$ BM). The $\langle \Delta U\rangle$'s may be compared with those of analogous dithiocarbamate complexes showing $t_{2g}^6 e_g^n$ electronic configuration ($n = 2, 4$). A weighted average from the last three entries in Table 4 is $0{\cdot}0035\,(9)$ Å^2 and supports the impression conveyed by the scatterplot, namely that the $\langle \Delta U\rangle$'s for high-spin Fe complexes are indeed larger than those for the corresponding low-spin complexes. This must be interpreted to mean that the stretching-force constants for the low-spin state with no electrons in σ-antibonding (e_g) molecular orbitals are larger than those for the high-spin state with two electrons in σ-antibonding orbitals. This is consistent with infrared evidence given by Butcher, Ferraro & Sinn (1976).

The maximum of the distribution is found between the extremes of pure l.s. and pure h.s. behaviour at $\langle d\rangle \sim 2{\cdot}38$ Å. If it is assumed that no intermediate spin state (corresponding to a $t_{2g}^4 e_g^1$ electronic configuration) is involved, this part of the distribution relates to situations of either dynamic equilibrium or static disorder with half the molecules in the low-spin state and the other half in the high-spin state.

An outlier is found in Fig. 3 at $\langle d\rangle = 2{\cdot}396$ Å and $\langle \Delta U\rangle = -0{\cdot}0019$ Å^2 [entry (3) in Tables 1 and 3]. The experimental details (Table 1) reveal that the X-ray diffraction data were obtained with Cu $K\alpha$ radiation, but were refined without taking the sizeable anomalous-dispersion corrections into account. For Fe, $f' = -1{\cdot}179$, $f'' = 3{\cdot}204$ and for S, $f' = 0{\cdot}319$, $f'' = 0{\cdot}557$. At the limit of the data ($\sin\theta/\lambda \sim 0{\cdot}61$ Å^{-1}) the resulting absolute error in the real part of the scattering factor for Fe is ~12%, for S ~5%; at $\sin\theta/\lambda = 0$ Å^{-1} it is still ~5% and ~2% respectively. Because of the omission, the scattering factor of Fe used in the analysis was systematically too high while that of S was too low. This deficiency is partly compensated for by increasing U(Fe) and decreasing U(S), making $\Delta U(z) = U_{\rm S}(z) - U_{\rm Fe}(z)$ too small, as observed. Thus the outlier in no way invalidates the observed correlation, since it is due to an inadequate model of the scattering process. Entry (3) represents the only example of our experiment with Fe, Co or Cu radiation in which no anomalous-dispersion correction, either f' or f'', was included in the refinement (Tables 1 and 2). The effect on U of neglecting f' and f'' is much smaller for data obtained with Mo radiation.

The data in Fig. 1 have been analysed by least-squares methods assuming the simplest model that seemed adequate, a quadratic dependence of $\langle \Delta U\rangle$ on $\langle d\rangle$. Using unit weights, the result is (e.s.d.'s in parentheses)

$$\langle \Delta U\rangle(\text{Å}^2) = -5{\cdot}37124 + 4{\cdot}51940\,(373)\langle d\rangle(\text{Å}) - 0{\cdot}94932\,(9897)\langle d\rangle^2(\text{Å}^2)$$

and using $w = 1/\langle\sigma(\Delta U)\rangle^2$,

$$\langle \Delta U\rangle(\text{Å}^2) = -5{\cdot}00985 + 4{\cdot}21127\,(228)\langle d\rangle(\text{Å}) - 0{\cdot}88373\,(7938)\langle d\rangle^2(\text{Å}^2);$$

correlation coefficients are $r^2 = 0{\cdot}78$ and $0{\cdot}83$ respectively.

Before proceeding to a theoretical analysis of these correlations, the distance parameters in Table 3 will be analysed for other structural changes accompanying the l.s.–h.s. transition.

Results: coordination geometry of the fragment [Fe(S$_2$CN)$_3$]

The distance parameters d(Fe–S), d(S···S), d(S–C) and d(C–N) in Table 3 were examined by factor analysis (Murray-Rust & Motherwell, 1978) using the *Statistical Package for the Social Sciences* (Nie, Hull, Jenkins, Steinbrenner & Bent, 1975). The results are shown in Table 5. Univariate statistics show the Fe–S distance to have the largest scatter, the overall standard deviation being an order of magnitude larger than e.s.d.'s from individual structures (Table 3). This also holds, albeit less clearly, for the S···S distance, but not for the S–C and C–N distances. Bivariate statistics show only one significant factor if the usual criteria are applied (eigenvalues > 1). This factor reveals that a change in the Fe–S distance by $+0{\cdot}87\sigma = 0{\cdot}045$ Å (Table 5) is accompanied by changes of d(S···S) by $+0{\cdot}90\sigma = 0{\cdot}027$ Å, of d(C–S) by $+0{\cdot}77\sigma = 0{\cdot}006$ Å and of d(C–N) by $-0{\cdot}84\sigma = -0{\cdot}008$ Å. The factor accounts for 72% of the total variance, about three times the value expected if the variance were distributed equally among the four factors. The coupling of the changes in distances is as expected on chemical grounds and partial correlations have been mentioned in almost every one of the

Table 5. *Results of factor analysis on distance parameters in* Fe$^{\rm III}$ *complexes*

(1) Univariate statistics (means and standard deviations)

d(Fe–S)	2·372 (52) Å	d(S···S)	2·861 (30) Å
d(S–C)	1·713 (8)	d(C–N)	1·323 (10)

(2) Bivariate statistics*

Eigenvalue	Components of eigenvector Fe–S	S···S	S–C	C–N	Variance
2·86	0·87	0·90	0·77	−0·84	0·72
0·85	0·46	0·41	−0·55	0·41	0·21

* Distances (Fig. 4) for each of the 35 molecules are represented as deviations from the respective means expressed in units of the corresponding standard deviations and considered as coordinates of a point in four-dimensional space. Principal axes of the four-dimensional distribution of points are calculated and given with the convention that the sum of the squared components equals the eigenvalue.

Table 6. *Bibliography of* $[(XCS_2)_3M]$ *complexes*

For compounds included in the October 1982 version of the CSD the REFCODE is given.

(1)	DMTCFE02	Albertsson, J., Oskarsson, Å., Ståhl, K., Svensson, C. & Ymén, I. (1981). *Acta Cryst.* B**37**, 50–56.
(2)	DMTCFE01	Albertsson, I. & Oskarsson, Å. (1977). *Acta Cryst.* B**33**, 1871–1877.
(3)	DMTCFE	Same as (2).
(4)	DMTCFE03	Same as (1).
(5)	PYTCFF	Bereman, R. D., Churchill, M. R. & Nalewajek, D. (1979). *Inorg. Chem.* **18**, 3112–3117.
(6)	—	Healy, P. C. & White, A. H. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1163–1171.
(7)	PYCDFE10	Mitra, S., Raston, C. L. & White, A. H. (1978). *Aust. J. Chem.* **31**, 547–553.
(8), (9)	—	Albertsson, J. (1983). Personal communication.
(10)	PYTCFE	Sinn, E. (1976). *Inorg. Chem.* **15**, 369–375.
(11)	DETCFE01	Leipoldt, J. G. & Coppens, P. (1973). *Inorg. Chem.* **12**, 2269–2274.
(12)	DETCFE	Same as (11).
(13)	MTCFET	Butcher, R. J. & Sinn, E. (1976). *J. Am. Chem. Soc.* **98**, 5159–5168.
(14)–(17)	—	Ståhl, K. (1983). *Acta Cryst.* B**39**, 612–620.
(18)	MRDTFE	Healy, P. C. & Sinn, E. (1975). *Inorg. Chem.* **14**, 109–115.
(19)	—	Ståhl, K. (1983). *Inorg. Chim. Acta*, **75** 85–91.
(20)	MORTFE	Same as (13).
(21)	MORTFF	Cukauskas, E. J., Deaver, B. S. Jr & Sinn, E. (1977). *J. Chem. Phys.* **67**, 1257–1266.
(22)	MCDTFE	Butcher, R. J. & Sinn, E. (1976). *J. Am. Chem. Soc.* **98**, 2440–2449.
(23)	HETCFE01	Albertsson, J., Oskarsson, Å. & Nygren, M. (1979). *Acta Cryst.* B**35**, 1473–1476.
(24)	HETCFE	Same as (23).
(25)	MPDCFE	Same as (6).
(26), (27)	—	Albertsson, J., Oskarsson, Å. & Ståhl, K. (1982). *Acta Chem. Scand. Ser. A*, **36**, 783–795.
(28)	BUSCFE	Hoskins, B. F. & Kelly, B. P. (1968). *Chem. Commun.* p. 1517; Hoskins, B. F. (1983). Personal communication.
(29)	BTCFEB	Mitra, S., Raston, C. L. & White, A. H. (1976). *Aust. J. Chem.* **29**, 1899–1904.
(30)	BZTCFE11	Albertsson, J., Elding, I. & Oskarsson, Å. (1979). *Acta Chem. Scand. Ser. A*, **33**, 703–717.
(31)	BZTCFE10	Same as (30).
(32)	EXANFE	Hoskins, B. F. & Kelly, B. P. (1970). *Chem. Commun.* pp. 45–46; Hoskins, B. F. (1983). Personal communication.
(33)	BTXANI	Lewis, D. F., Lippard, S. J. & Zubieta, J. A. (1972). *Inorg. Chem.* **11**, 823–828.
(34)	MOTCCR	Butcher, R. J. & Sinn, E. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2517–2522.
(35)	MCDTCR	Same as (22).
(36)	DEDTFE10	Coucouvanis, D., Hollander, F. J. & Pedelty, R. (1977). *Inorg. Chem.* **16**, 2691–2696.
(37)	ETDCCO01	Merlino, S. (1968). *Acta Cryst.* B**24**, 1441–1448.
(38)	ETDCCO	Brennan, T. & Bernal, I. (1969). *J. Phys. Chem.* **73**, 443–445.
(39)	BDTCBR	Fackler, J. P. Jr, Avdeef, A. & Fischer, R. G. Jr (1973). *J. Am. Chem. Soc.* **95**, 774–782.
(40)	BTCNIA	Christidis, P. C. & Rentzeperis, P. J. (1978). *Acta Cryst.* B**34**, 2141–2146.
(41)	CHTNIA	Stergioudis, G. A., Christidis, P. C. & Rentzeperis, P. J. (1979). *Acta Cryst.* B**35** 616–620.
(42)	EDTCGA	Dymock, K., Palenik, G. J., Slezak, J., Raston, C. L. & White, A. H. (1976). *J. Chem. Soc. Dalton Trans.* pp. 28–32.

papers referenced in Table 6. Pairwise correlations between structural parameters, magnetic properties and ESCA measurements are discussed in detail by Ståhl & Ymén (1983).

From the data in Tables 3 and 5, prototype coordination geometries of the dithiocarbamate ligand to $\mathrm{Fe^{III}}$ can be defined for the pure l.s. and h.s. cases: d(Fe–S) is fixed to 2·30 Å for the l.s. case [d(l.s.)] and to 2·45 Å for the h.s. case [d(h.s.); see also Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1981]; the values corresponding to the two extremes for the other distances are then obtained from the components of the first eigenvalue and the standard deviations in Table 5. Fig. 4 summarizes the results and shows that the S atoms do not move along the Fe–S bond, but rather along a line which is inclined by 20·4 to 21·8° to the Fe–S bonds when a molecule undergoes l.s.–h.s. transition.

Influence of l.s.–h.s. transition on $\Delta U(z)$

The rate of spin cross-over has been estimated to be in the range 10^7–$10^{10}\,\mathrm{s^{-1}}$ (Hall & Hendrickson, 1976). It has also been shown that cross-over in one molecule induces a transition in at most one neighbouring molecule, *i.e.* cooperativity effects are very small (Ståhl, 1983). This implies that an X-ray quantum being scattered by the crystal encounters an essentially random distribution of a fraction p of the molecules in the l.s. state and of $(1-p)$ of the molecules in the h.s. state. For such a distribution the average distance $\langle d(\text{Fe–S})\rangle$ is

$$\langle d(\text{Fe–S})\rangle = pd(\text{l.s.}) + (1-p)d(\text{h.s.}).$$

The influence of the spin equilibrium on $\Delta U(z)$ is modelled as follows. A normalized Gaussian distribution with halfwidth ΔU(l.s.) is placed at a distance d(l.s.) from Fe and weighted with the factor p. It represents the S atoms in the low-spin complexes. Another Gaussian, this time with halfwidth ΔU(h.s.), is placed at d(h.s.) from Fe and weighted with $(1-p)$. It represents the S atoms in the high-spin complexes. The second moment of the resulting non-Gaussian distribution of S atoms may then be calculated as a function of p or $\langle d(\text{Fe–S})\rangle$ and compared to experimental values of $\langle \Delta U\rangle$.

Defining the differences between the mean and the l.s. or h.s. distances respectively as

$$\Delta(\text{l.s.}) = \langle d(\text{Fe–S})\rangle - d(\text{l.s.})$$
$$\Delta(\text{h.s.}) = d(\text{h.s.}) - \langle d(\text{Fe–S})\rangle$$

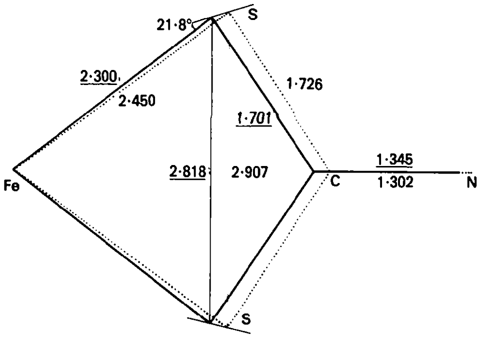

Fig. 4. Prototype coordination geometries of the dithiocarbamate ligand to iron(III) in the low-spin (full line) and high-spin (dotted line) state derived from factor analysis (Table 5). Distances pertaining to the low-spin state are underlined.

the model for $\Delta U(z)$ has the following algebraic form:

$$\begin{aligned}\Delta U = \int_{-\infty}^{+\infty} & (p[2\pi\Delta U(\mathrm{l.s.})]^{-1/2} \\ & \times \exp\{-[z-\Delta(\mathrm{l.s.})]^2/[2\Delta U(\mathrm{l.s.})]\} \\ & +(1-p)[2\pi\Delta U(\mathrm{h.s.})]^{-1/2} \\ & \times \exp\{-[z-\Delta(\mathrm{h.s.})]^2/[2\Delta U(\mathrm{h.s.})]\})z^2\,\mathrm{d}z \\ = {} & p[\Delta U(\mathrm{l.s.})+\Delta^2(\mathrm{l.s.})] \\ & +(1-p)[\Delta U(\mathrm{h.s.})+\Delta^2(\mathrm{h.s.})].\end{aligned}$$

In this approximation theoretical $\Delta U(z)$'s are composed of two independent contributions: one which originates from the pure l.s. and pure h.s. complexes [ΔU(l.s.) and ΔU(h.s.)], and another which arises from the differences Δ(l.s.) and Δ(h.s.). For $p=0$ or 1 the Δ^2 terms vanish and only one ΔU term remains. On evaluating p in terms of $d(\mathrm{l.s.}) = 2\cdot30$ Å, $d(\mathrm{h.s.}) = 2\cdot45$ Å and $\langle d(\text{Fe–S})\rangle$, transforming to $\delta = \langle d(\text{Fe–S})\rangle - 2\cdot375$ Å, *i.e.* to the centre of the observed range of distances, and introducing typical values $\Delta U(\mathrm{l.s.}) = 0\cdot0017$ Å^2, $\Delta U(\mathrm{h.s.}) = 0\cdot0035$ Å^2 as discussed in *Results: vibrational amplitudes*,

$$\Delta U(\text{Å}^2) = 0\cdot0082 + 0\cdot0120\delta(\text{Å}) - \delta^2(\text{Å}^2).$$

This model does not take into account the mean angle $\gamma \sim 21\cdot1°$ between the direction of motion of S and the Fe–S bonds (Fig. 4). With this correction

$$\begin{aligned}\Delta U(\text{Å}^2) &= p[\Delta U(\mathrm{l.s.}) + \cos\gamma\Delta^2(\mathrm{l.s.})] \\ &\quad +(1-p)[\Delta U(\mathrm{h.s.}) + \cos\gamma\Delta^2(\mathrm{h.s.})] \\ &= 0\cdot0078 + 0\cdot0120\delta(\text{Å}) - 0\cdot93\delta^2(\text{Å}^2).\end{aligned}$$

Both models are in excellent agreement with the results of the unweighted and weighted regressions, which are, in terms of δ,

$$\langle\Delta\rangle(\text{Å}^2) = 0\cdot0076 + 0\cdot0102\,(35)\delta(\text{Å}) - 0\cdot95\,(10)\delta^2(\text{Å}^2)$$
$$\langle\Delta\rangle(\text{Å}^2) = 0\cdot0071 + 0\cdot0136\,(22)\delta(\text{Å}) - 0\cdot88\,(8)\delta^2(\text{Å}^2).$$

It is concluded that distances and ΔU's derived from X-ray diffraction data on tris(dithiocarbamato)-iron(III) complexes can be fully explained in terms of a mixture of only two spin states in the crystal, namely a $t_{2g}^5 e_g^0$ low-spin state and a $t_{2g}^3 e_g^2$ high-spin state; no intermediate $t_{2g}^4 e_g^1$ spin state needs to be invoked (Butcher & Sinn, 1976). Alternatively, it could be argued that magnetic and spectroscopic evidence are sufficient by themselves to demonstrate the presence of only two spin states (Hall & Hendrickson, 1976; Eisman, Reiff, Butcher & Sinn, 1981; Ståhl, 1983). On these premises the striking agreement between the model and the observed correlation shows that in spite of their small magnitudes the ΔU's represent real physical information.

Discussion

The above analysis of ΔU's seems to be one of the rare cases where justification is needed for agreement between experiment and theory rather than for disagreement. Specifically, it could be argued that the ΔU's show mainly random error and are surprisingly little affected by systematic error.

First it has to be noted that the study was performed with Fe and S atoms, for which the scattering of 18 and 10 core electrons, respectively, dominates over that of the valence electrons. Thus the ΔU values for the Fe–S bonds are determined relatively more accurately than those for the C–S and N–C bonds. The ΔU's along each of the three bonds averaged over all entries in Table 3 are respectively 0·0047, 0·0033, −0·0016 Å^2 with corresponding average e.s.d.'s from the diffraction experiments of 0·0020, 0·0051, 0·0066 Å^2. Even for the Fe–S bond the ratio of the mean ΔU to the mean e.s.d. is only 2·35, suggesting a result of only moderate significance. However, ΔU(Fe–S) shows a clear quadratic dependence on d(Fe–S) with $r^2 = 0\cdot78$ whereas ΔU(C–S) and ΔU(N–C) show no such dependence, either on d(C–S) and d(N–C) or on d(Fe–S); corresponding correlation coefficients are in the range $r^2 = 0\cdot001$ to 0·20.

Second, the quality of ΔU's depends on the inclusion of anomalous-scattering corrections in the model of the scattering process. The effect of neglecting such corrections has been demonstrated in *Results: vibrational amplitudes.*

Neglect of absorption effects is a further source of error in the U's. This correction has not been applied for entry (20) and probably not for entry (28) (Table 1). The corresponding ΔU's, however, do not deviate from the correlation curve any more than do the ΔU's based on data corrected for absorption (Table 3 and Fig. 3). Probably the error may be represented to first order by a tensor typical of the crystal specimen used for the diffraction experiment. The refined vibrational parameters will then be the sum of two terms, an intrinsic vibrational contribution for each atom i and a contribution compensating for the systematic error due to the neglect of the absorption correction;

$$\mathbf{U}^i(\mathrm{obs}) = \mathbf{U}^i(\mathrm{intrinsic}) + \mathbf{U}(\text{systematic error}).$$

The contribution from the second term will always cancel out in the ΔU's. An analogous argument has been shown to apply if corrections for thermal diffuse scattering are neglected (Stevenson & Harada, 1983). Thus, while the $\mathbf{U}^i$'s themselves – their absolute value as well as their anisotropy – could well be severely in error, the ΔU's represent more reliable physical information. As an aside it may be noted that for rigid-body analysis or modified rigid-body analysis the term **U**(systematic error) affects the translation tensor **T** but not the libration tensor **L** or the amplitudes of internal torsional motions. Indeed, in their study of naphthalene at five different temperatures, Brock & Dunitz (1982) note 'that, on the whole, the agreement between theory [lattice-dynamical calculations based on atom–atom potentials] and experiment is better for the **L**'s than for the **T**'s'. A similar judgment might apply to the amplitudes of internal torsional motions derived by Trueblood & Dunitz (1983).

Given a range of R values between 0·028 and 0·13, it is of interest to see whether the agreement between observed and calculated ΔU's depends upon the accuracy of the structure determination. It does not: the three largest deviations ($>0{\cdot}0020$ Å^2) from the correlation curve (Fig. 3) are +0·0023, +0·0025 and +0·0025 Å^2 for entries (1), (14) and (24) (Table 3) with R values of 0·046, 0·055 and 0·067 respectively (Table 1). On the other hand, the three points from film data corresponding to entries (6), (25) and (28) with R values of 0·13, 0·087 and 0·075, apparently poor structural studies, show deviations of only −0·0002, −0·0007 and +0·0010 Å^2 respectively.

The site symmetry of Fe is 1 in most structures in our survey and there is no reason for the Fe atom to stay fixed in place when a complex increases its diameter by 0·3 Å during the spin transition; more generally, rigid-body translation (and rotation) of the complex during l.s.–h.s. transition cannot be excluded (Scheringer & Fadini, 1979). In the model discussed earlier it was implicitly assumed, however, that Fe has the same position in both spin states. The effects due to a shift b of the Fe position along an Fe–S bond are easily calculated for a linear, symmetric arrangement S(1)–Fe–S(2); it is found that for $b < d$(Fe–S), ΔU[S(1)] and ΔU[S(2)] do depend on b but the average $\{\Delta U[\mathrm{S}(1)]+\Delta U[\mathrm{S}(2)]\}/2$ does not. Thus the averaging of independent ΔU's for each molecule serves a dual purpose: not only does it reduce random error, but it also eliminates systematic effects due to spin-dependent differences in the Fe position. Indeed, if the ΔU along each independent Fe–S bond in each molecule is plotted against the corresponding Fe–S distance the correlation seen so clearly in Fig. 3 is hardly discernible.

In a number of cases the same compound has been studied at several temperatures (Table 1) with the intention of investigating the effects of the l.s.–h.s. *equilibrium* on the **U**'s. In one case the authors state 'clearly, no conclusion can be drawn from the present temperature factors as to the nature of the magnetic transition' (Leipoldt & Coppens, 1973). Inspection of the vibrational parameters shows that the **U**'s of both Fe and S are affected by temperature in all directions of space, and that these changes are ~5 times as large as those induced by the spin transition which affects **U**'s of S mainly along the direction of the Fe–S bond. Indeed, it is for this reason that the spin transition can be followed more clearly through ΔU's than **U**'s.

Conclusions

In summary, the ΔU values – in spite of their small magnitudes – contain significant physical information. This information seems to be independent of the radiation used, the absorption properties of the crystal and the accuracy of structure determination as gauged from R values. However, it does depend on the corrections for anomalous scattering. Furthermore, averaging over chemically equivalent bonds helps to reduce random error and, in some cases, to eliminate systematic effects arising from coupling of rigid-body motions to internal motions of the molecule.

It was shown that a less stringent form of Hirshfeld's rigid-bond postulate applies to coordination complexes; diffraction and spectroscopic data indicate typical values of $\Delta U(z)$ up to 0·003 Å^2. The modified postulate is powerful enough to distinguish between normal vibrational behaviour and dynamic or static disorder. An example of the latter is compositional and positional disorder in minerals. Specifically, the Al/Si ordering in Al-substituted silicates is usually judged on the basis of the observed metal–oxygen distances which range from ~1·61 Å for an Si–O bond to ~1·74 Å for an Al–O bond (Shannon, 1976). It would seem that ΔU values for such compounds could provide additional information about the detailed nature of the disorder.

The present study has investigated effects of disorder on the harmonic (anisotropic) vibrational parameters. However, the atomic probability density functions in such cases need not be Gaussian, and may sometimes be better described by including anharmonic vibrational parameters in the model of the electron density function. Several algorithms incorporating these features have been developed and a corresponding program package is now available (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). The physical significance of the results obtained from anharmonic models could be analysed similarly by extending the methods described in this paper.

It is refreshingly pleasant to acknowledge unstinted and prompt cooperation from Professors J. Albertsson and B. F. Hoskins who courteously provided us data as yet unpublished, without any reservation or delay. We thank Professor K. N. Trueblood for a copy of the latest version of his program *THMB* and for discussion. We acknowledge suggestions to improve the manuscript by Professors Dunitz, Hirshfeld, Scheringer and Wondratschek, and an anonymous referee. This work was supported by the 'Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung'.

References

Albertsson, J., Oskarsson, Å., Ståhl, K., Svensson, C. & Ymén, I. (1981). *Acta Cryst.* **B37**, 50–56.

Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* **B35**, 2331–2339.

Ammeter, J. H., Bürgi, H.-B., Gamp, E., Meyer-Sandrin, V. & Jensen, W. P. (1979). *Inorg. Chem.* **18**, 733–750.

Bergerhoff, G., Hundt, R. & Sievers, R. (1982). ICSD. Inorganic Crystal Structure Database. Institut für anorganische Chemie der Universität Bonn.

Bernhard, P., Bürgi, H.-B., Hauser, J., Lehmann, H. & Ludi, A. (1982). *Inorg. Chem.* **21**, 3936–3941.

Bernhard, P. & Ludi, A. (1984). *Inorg. Chem.* In the press.

Bonadeo, H. & Burgos, E. (1982). *Acta Cryst.* **A38**, 29–33.

Brock, C. P. & Dunitz, J. D. (1982). *Acta Cryst.* **B38**, 2218–2228.

Bürgi, H.-B. (1982). In *Computational Crystallography*, edited by D. Sayre. Oxford: Clarendon Press.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142–146.

Butcher, R. J., Ferraro, J. R. & Sinn, E. (1976). *Inorg. Chem.* **15**, 2077–2079.

Butcher, R. J. & Sinn, E. (1976). *J. Am. Chem. Soc.* **98**, 2440–2449.

Cambi, L. & Szegö, L. (1931). *Ber. Dtsch. Chem. Ges.* **64**, 2591–2598.

Cambi, L. & Szegö, L. (1933). *Ber. Dtsch. Chem. Ges.* **66**, 656–661.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.

Cyvin, B. N., Cyvin, S. J., Schmidt, K. H., Müller, A. & Brunvoll, J. (1976). *J. Mol. Struct.* **32**, 269–278.

Dunitz, J. D. & White, D. N. J. (1973). *Acta Cryst.* **A29**, 93–94.

Eisman, G. A., Reiff, W. M., Butcher, R. J. & Sinn, E. (1981). *Inorg. Chem.* **20**, 3484–3486.

Ewald, A. H., Martin, R. L., Ross, I. G. & White, A. H. (1964). *Proc. R. Soc. London Ser. A*, **280**, 235–241.

Gavezotti, A. & Simonetta, M. (1982). *Chem. Rev.* **82**, 1–13.

Gramaccioli, C. M., Filippini, G. & Simonetta, M. (1982). *Acta Cryst.* **A38**, 350–356.

Hall, G. R. & Hendrickson, D. N. (1976). *Inorg. Chem.* **15**, 607–618.

Harel, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* **B31**, 162–172.

Herzberg, G. (1945). *Molecular Spectra and Molecular Structure*, p. 173. New York: Van Nostrand.

Hirshfeld, F. L. (1976). *Acta Cryst.* **A32**, 239–244.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.

Johnson, C. K. (1970*a*). In *Thermal Neutron Diffraction*, edited by B. T. M. Willis. Oxford Univ. Press.

Johnson, C. K. (1970*b*). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 220–226. Copenhagen: Munksgaard.

Leipoldt, J. G. & Coppens, P. (1973). *Inorg. Chem.* **12**, 2269–2274.

Murray-Rust, P. & Motherwell, S. (1978). *Acta Cryst.* **B34**, 2534–2546.

Nie, N. H., Hull, C. H., Jenkins, J. G., Steinbrenner, K. & Bent, D. H. (1975). *SPSS. Statistical Package for the Social Sciences.* New York: McGraw-Hill.

Scheringer, C. & Fadini, A. (1979). *Acta Cryst.* **A35**, 610–613.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.

Ståhl, K. (1983). *On the Magnetic Properties of Solid Tris-(dithiocarbamato)iron*(III) *Compounds*, pp. 26–33. Dissertation, Univ. of Lund.

Ståhl, K. & Ymén, I. (1983). *Acta Chem. Scand. Ser. A*, **37**. In the press.

Stevenson, A. W. & Harada, J. (1983). *Acta Cryst.* **A39**, 202–207.

Trueblood, K. N. (1982). Private communication.

Trueblood, K. N. & Dunitz, J. D. (1983). *Acta Cryst.* **B39**, 120–133.

Vedani, A. (1981). *Statische und dynamische Jahn–Teller Verzerrungen in Mangan*(III)- *und Kupfer*(II)-*Verbindungen.* Dissertation, Univ. Zürich.

White, A. H., Roper, R., Kokot, E., Waterman, H. & Martin, R. L. (1964). *Aust. J. Chem.* **17**, 294–303.

Willis, B. T. M. (1982). In *Computational Crystallography*, edited by D. Sayre. Oxford: Clarendon Press.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge Univ. Press.

Zucker, U. H., Perenthaler, E., Kuhs, W. F., Bachmann, R. & Schulz, H. (1983). *J. Appl. Cryst.* **16**, 358.