Metal Ligand Bond Contraction and Possible Spin–Orbit Induced Jahn–Teller Distortion in the Iron(III) Dialkyldithiocarbamate 'Crossover' System

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Summary Comparison of the crystal structures of high- and low-spin iron(III) dialkyldithiocarbamate complexes, $[Fe(CS_2{\cdot}NR_2)_3]$, reveals (*a*) the predicted difference (0·1 Å) in metal–sulphur bond length and (*b*) an unusual distortion from D_3 to C_3 symmetry in the low-spin complex, attributed to spin–orbit interactions in the ground state.

TEMPERATURE dependent studies of the magnetic moment μ (B.M.) of tris-(*NN*-dialkyldithiocarbamato)iron(III) complexes, $[Fe(CS_2{\cdot}NR_2)_3]$, show the existence of almost equi-energetic ground states ($^6A_1$ and $^2T_{2g}$ in the O_h approximation).[1] Which state is lower depends on the choice of R.[2] Pressure dependent studies of μ show a molecular contraction of *ca.* 4 cm^3 mol^{-1} as a $^6A_1$ ground state ($t_{2g}^3e_g^2$) passes to a $^2T_{2g}$ ground state (t_{2g}^5). As a comparable contraction does not occur in the cobalt(III) analogues ($^1A_1$, t_{2g}^6), this is attributed to shrinkage of the FeS_6 core, due to a contraction of *ca.* 0·1 Å in the Fe–S linkage.[1]

Preliminary results have been reported by Hoskins and Kelly for structure determinations on the predominantly high-spin tris-(*NN*-di-n-butyldithiocarbamato)iron(III) (A)[3] and the related, predominantly low-spin tris-(*O*-ethylxanthato)iron(III) (B).[4] We have investigated the room temperature structures of the purely high-spin tris(tetramethylenedithiocarbamato)iron(III) (C) and the low-spin tris-(*N*-methyl-*N*-phenyldithiocarbamato)iron(III) (D). The relevant crystallographic data of the MS_6 core for these four complexes are given in the Table. Included also are the electronic ground states of these complexes and the room-temperature magnetic moments. For comparison, we have included structural data available on similar complexes of cobalt(III), (E)[6] and (F).[7]

From these results, we draw three conclusions regarding the central MS_6 core. (i) Both our data and those of Hoskins indicate a contraction of at least 0·1 Å in the mean Fe–S distance on passing from the high-spin to the low-spin

TABLE

Properties of the complexes (A)—(F)

Cpd.	Formula	Space group	*a*	*b*	*c*	*β*°	Mean M–S bond-lengths	2*θ*	*ζ*	*μ*	Ground state O_h	Ground state D_3	Ref.
(A)	$[Fe(CS_2.NBu^n_2)_3]$	*C*2/*c*	22·49	10·48	18·41	120·8	2·42	33·2	93·5	5·3	$^6A_1$	^6A	3[a]
(B)	$[Fe(CS_2.OEt)_3]$	*R*3	14·91		13·31		2·308 2·326	41·2	94·1	2·7	$^2T_{2g}$	^2E ^2A	4
(C)	$[Fe(CS_2.N[CH_2]_4)_3]$	$P2_1/n$	16·23	14·53	10·22	90·3	2·41	38·6	93·6	5·9	$^6A_1$	^6A	[b]
(D)	$[Fe\{CS_2.N(Me)(Ph)\}_3]$	$P2_1/a$	25·3	12·9	9·5	116·2	2·30 2·33	40·4	94·1	2·9	^2T_2g	^2E ^2A	[b]
(E)	$[Co(CS_2.NEt_2)_3]$	*C*2/*c*	14·10	10·26	17·02	110·1	2·26	43·0	94·2	—	$^1A_1$	^1A	6
(F)	$[Co(CS_2.OEt)_3]$	$R\bar{3}$	14·87		13·22		2·276 2·277	42·4	94·3	—	$^1A_1$	^1A	7

[a] These data differ from those in ref. 3 and derive from revised results kindly supplied by B. F. Hoskins. [b] This work.

form, in agreement with the previous pressure–magnetism studies

(ii) The geometry of the FeS_6 core for the high-spin systems approximates to point group D_3 (Figure 1) rather

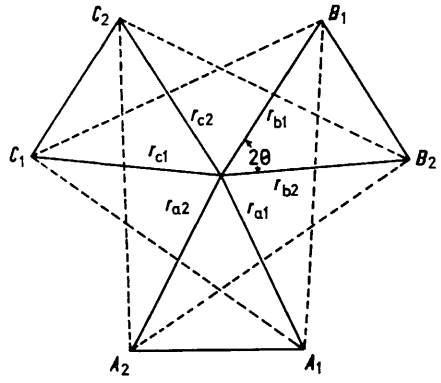

FIGURE 1 *Model* FeS_6 *molecular core viewed down the* C_3 *axis. It is considered as a pair of parallel equilateral triangles of sulphur atoms* (Sa1 Sb1, Sc1) (Sa2, Sb2, Sc2) *arising from ligands* a, b, *and* c *and defined by metal–sulphur distances* r_{i1} *and* r_{i2} *and angle* 2θ, *the axial projection of the deviation of the molecule from the trigonal prism extreme.*

than O_h This trigonal distortion is to be expected from the geometrical constraint applied to the system by the four membered rings and can be characterized by two parameters 2θ and ζ 2θ is the angle of twist (relative to the C_3 axis) between the upper and lower triangles (Sa1, Sb1, Sc1), (Sa2, Sb2, Sc2) of sulphur atoms (Figure 1) ζ is the mean pyramidal angle of either FeS_3 system (*e g* the S11–Fe–S31 angle) and describes the degree of distortion along the C_3 axis In the O_h limit $2\theta = 60°$, $\zeta = 90°$

From the Table, it can be seen that ζ is relatively constant as the compounds tend towards the high-spin limit, and that 2θ tends slightly towards the trigonal prismatic The small magnitude of these changes suggests that the FeS_6 angular contraction is affected only indirectly by the electronic ground state *via* the Fe–S bond contraction

(iii) In the low-spin complexes, (B) and (D), the molecular geometry approximates to the point group C_3, *i e* $\bar{r}_1$ and $\bar{r}_1'$ (Figure 1) differ significantly (by *ca* 0 03 Å) It is improbable that distortion of this type in both (B) and (D) is due to ligand effects or packing forces as one might then expect a similar phenomenon in (E) and (F), particularly (F) which is isomorphous with (B) It is likely that the distortion is electronic in origin and due to the $^2T_{2g}$ state which is susceptible to Jahn–Teller and spin–orbit interactions In point group D_3, however, the $^2T_{2g}$ state becomes ^2A and ^2E and cannot be split further, unless the three-fold axis is destroyed

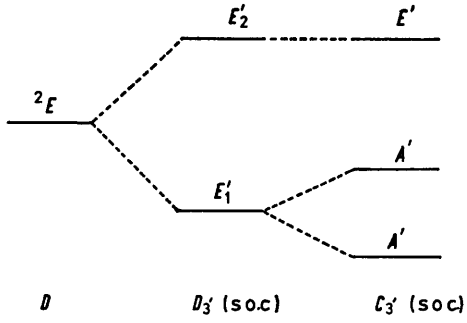

FIGURE 2 *Diagram showing the splitting of the* ^2E *state in point group* D_3 *as the symmetry is lowered progressively by* (a) *spin–orbit coupling* (*to* D_3'), (b) *expansion of the lower triangle of sulphur atoms relative to the upper* (*to* C_3')

Inclusion of the spin–orbit coupling operator results in the E state of D_3 splitting to E_1' and E_2' in the double group D_3' Further distortion to C_3' splits the E_1' state into two A' states (Figure 2) It hence seems that spin–orbit coupling in the lowest thermally accessible states provides a mechanism for a form of Jahn–Teller distortion to occur The magnitude observed surprises us

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