Magnetic Properties of Iron(II) near the $^5T_2$–$^1A_1$ Crossover

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A series of iron(II) complexes which lie near the high spin–low spin crossover ($FeL_2X_2.nH_2O$, where X is NCS or NCSe and L is a ring-substituted analogue of 1,10-phenanthroline or 2,2′-bipyridyl) have been prepared and their magnetic and spectroscopic properties investigated. Small modifications in the molecules are found to produce startling effects on the properties, and the various members of the series illustrate many kinds of ' crossover ' behaviour. Some of the complexes have nearly equienergetic high spin and low spin states, both of which are thermally populated while some exhibit complete transitions between the two spin states within very narrow temperature ranges; the behaviour of some of the complexes falls in between these two extremes, while others have temperature independent moments, intermediate between high and low spin values, attributable to a triplet ground state.

In recent years, a number of workers have shown interest in the magnetic properties of iron(II) complexes near the high spin ($^5T_2$)–low spin ($^1A_1$) crossover.[1-9] Their studies have not led to complete understanding of the phenomenon observed, but the nature of the problem has been greatly clarified. The ground state

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crossover situations of iron(II) fall into two distinct classes: (I) those with magnetic properties that can be described by appropriate theoretical equations for a ' true ' or classical crossover with thermally accessible high and low spin states,[2,4-6] and (II) those which defy such description because the magnetic moment changes far too abruptly to be in credible accord with any crossover model.[7-10]

A further class of ' anomalous ' magnetic properties should be recognised, *viz*, (III) intermediate magnetic moments which are essentially independent of temperature and cannot be rationalised in terms of either a singlet or quintet ground state.[11] This could arise in a six-co-ordinate complex in which the symmetry is considerably distorted from octahedral such that splitting of the *e* orbital energies makes occupation of more than one of them unfavourable (Figure 1).

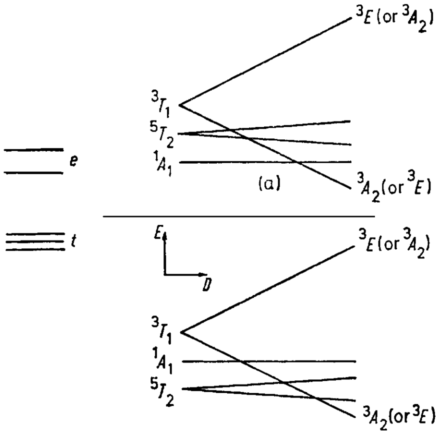

FIGURE 1 Distortion splitting of *e* set: $^3T_1$ (and $^3T_2$) is split; $^5T_2$ splits only when mixing with higher states is considered, or when t_2 orbitals split

A gradual increase in magnetic moment (μ_{eff}) with increasing temperature is readily explained in terms of increasing thermal population of the high spin state. Phenomenon (II) is suggestive of a second order phase change, although opinion varies on this point.[5,12-15] In both (I) and (II), significant and reproducible changes in magnetism, electronic and Mössbauer spectra readily demonstrate the existence of a crossover between two distinct ground spin states, even though the mechanism may be disputed, but temperature insensitive magnetic moments are normally taken as a sign of impurities rather than of intermediate spin states. Thus it must be carefully established that an intermediate μ_{eff} arises from a single species, and not from a fortuitous mixture.

We present here two series of complexes, each series having slight modifications of the ligand, which exhibit each of the three types of behaviour outlined above.

EXPERIMENTAL

Bis(5*R*-o-*phenanthroline*)*dithiocyanatoiron*(II) *Dihydrate*, (R = H, CH_3, Cl, NO_2, and C_6H_5 corresponds to L = phen, 5Me-phen, 5Cl-phen, $5NO_2$-phen, and 5Ph-phen respectively).—Ferrous alum (1·5 mmol) and 5R-*o*-phenanthroline (3 mmol) were dissolved in deoxygenated water (15 ml). Potassium thiocyanate (3 mmol dissolved in minimum of water) was added dropwise.[16] The precipitate which formed was collected, washed sparingly with ethanol, and finally with ether. The reaction was carried out under nitrogen to prevent oxidation to ferric iron.

Bis(*substituted-phenanthroline or bipyridyl*)*dithiocyanatoiron*(II) *Monohydrate* (bipy = 2,2′-bipyridyl; Me_2-bipy = 4,4′-dimethyl-2,2′-bipyridyl; Me_4-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline).—*Method* 1. The dihydrates above were heated under reflux in benzene. The change from red to purple occurred rapidly. The *red o*-phenanthroline complex $[Fe(o\text{-phen})_2(NCS)_2],2H_2O$ was heated in a drying pistol *in vacuo* at 180° (boiling 1,2-dichlorobenzene) until at constant weight. The red compound turned purple. Weight loss 3·7%, 2·9%; calculated for loss of one molecule of water 3·2%. No further weight loss observed even to 207°.

Method 2. The appropriate tris-complexes $(FeL_3)X_2,nH_2O$ were prepared as previously described [17-19] by reaction of a slight excess of the ligand L with ferrous sulphate and the potassium salt KX. The standard procedure [19] of refluxing these compounds in benzene or toluene was then followed. In each case water was removed by a water trap, but was not estimated since water has some solubility in benzene and toluene. The microcrystalline insoluble product was then filtered off, and the residual ligand recovered by evaporation of the solvent and estimated by weight as the anhydrous ligand. Recovery was high, though not 100% (Table 1). Microanalyses for C, H, and N were performed at the Microanalytical Laboratory, University of Otago, New Zealand. Hydrogen and nitrogen analyses were reliable and consistent. However, carbon analyses were more variable. Analytical data are given in Table 1.

Magnetic Measurements.—The magnetic susceptibilities were determined on three susceptometers: cryostat controlled Gouy and Faraday balances, both described elsewhere,[20] and a Newport variable temperature Gouy system with a Mettler H20 single balance pan. The possibility of magnetic field dependence was checked for each class of complexes by measurements at different field strengths and four different fields were used for each measurement on many of the complexes. In no case was there a significant magnetic field dependence. The sample holders were calibrated using the three standards $Hg[Co(SCN)_4]$, $[Ni(en)_3]S_2O_3$, and $CuSO_4,5H_2O$.[20] The accuracy of the temperatures in the cryostats was checked by comparison

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TABLE 1

Analytical data [a]

Complex	Calculated % C	Calculated % H	Calculated % N	Calculated % Fe	Found % C	Found % H	Found % N	Found % Fe
$Fe(phen)_2(NCS)_2,2H_2O$	55·55	3·5	14·8		55·05	3·6		
$Fe(phen)_2(NCS)_2,H_2O$	56·8	3·25	15·3		15·5	3·25	15·4	
$Fe(5NO_2\text{-}phen)_2(NCS)_2,2H_2O$	47·5	2·75	17·05		49·0	2·7	16·95	
$Fe(5NO_2\text{-}phen)_2(NCS)_2,H_2O$	48·8	2·5	17·5		51·05	2·75	16·85	
$Fe(5NO_2\text{-}phen)_2(NCS)_2,H_2O$ [b]				8·7				9·1
$Fe(5Me\text{-}phen)_2(NCS)_2,2H_2O$	56·45	4·05	14·1		57·95	4·05	14·15	
$Fe(5Me\text{-}phen)_2(NCS)_2,H_2O$	58·2	3·8	14·55		58·6	3·6	14·85	
$Fe(5Cl\text{-}phen)_2(NCS)_2,2H_2O$	48·9	2·8	13·15		50·3	2·8	13·15	
$Fe(5Cl\text{-}phen)_2(NCS)_2,H_2O$	50·05	2·6	13·55		50·7	2·5	14·1	
$Fe(5Cl\text{-}phen)_2(NCS)_2,H_2O$ [c]				9·0				9·2
$Fe(5Cl\text{-}phen)_2Cl_2$ [d]				10·0				9·6
$Fe(5Ph\text{-}phen)_2(NCS)_2,2H_2O$	63·35	3·9	11·7		61·4	3·9	11·75	
$Fe(Me_4\text{-}phen)_2(NCS)_2,H_2O$ [e]				8·4				8·5
$Fe(Me_4\text{-}phen)_2Cl_2$ [f]				9·3				8·9
$Fe(Me_2\text{-}bipy)_2(NCS)_2$ [g]				10·3				10·1
$Fe(Me_2\text{-}bipy)_2(NCSe)_2$ [h]	49·25	3·8	13·25	8·8	49·45	4·15	13·2	8·6

[a] All compounds prepared by method 1 except for those itemised below. [b–h] Prepared by method 2, using *ca.* 6—11 × 10^{-4} moles of $[FeL_3]X_2,nH_2O$. Ligand collected (as % of theoretical) 93, 78, 115, 90, 99, 97, and 100 for *b* through *h* respectively.

with the known temperature dependences of $CuSO_4,5H_2O$, $Hg[Co_6SCN)_4]$, and [Cu(salen)], and by direct measurement with a platinum resistance thermometer embedded in the sample cavity.

Differential Thermal Analysis.—A two compartment tube of similar size to the Gouy tube was placed inside the low-temperature cryostat. One section contained $\alpha\text{-}Al_2O_3$ as reference and another the complex under study. Copper–constantan thermocouples were embedded in each sample and connected to a Cambridge slide wire potentiometer type 44244/3 accurate to within 0·001 mV and a Tinsley Galvanometer type Sr4/45 with a deflection of 5 mm/μV. The temperature was allowed to drop (or rise) gradually but continuously and e.m.f. differences resulting between sample and reference were recorded against temperature. A total run (temperature range 200°) took one hour. Plots of thermocouple e.m.f. ∝ $(T_{\text{reference}} - T_{\text{sample}})$ against T are given in Figure 2.

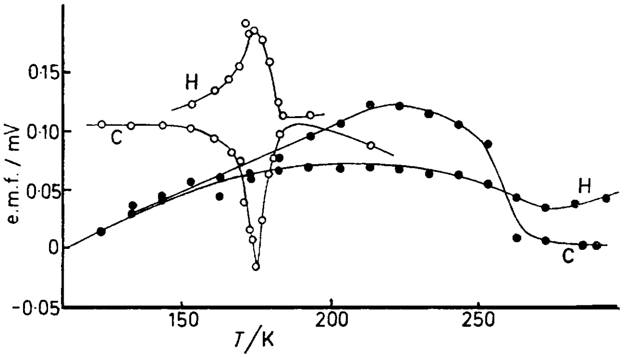

FIGURE 2 DTA curves (EMF ∝ $(T_{\text{sample}} - T_{\text{reference}})$ against T/K for $[Fe(phen)_2(NCS)_2],H_2O$ (○) and $[Fe\ (5Me\text{-}phen)_2(NCS)_2]H_2O$ (●); H = sample heating, C = sample cooling

X-Ray Powder Photographs.—Photographs were taken with a Phillips Debye Scherrer Camera using a Cu-K_α radiation.

Infrared Spectra.—Spectra were recorded on a Perkin-Elmer 337 grating instrument for Nujol mulls.

Mössbauer spectra were collected on a linear drive spectrometer. Data were computer-fitted to Lorentzian line shapes by a least squares procedure.

RESULTS AND DISCUSSION

Ferrous alum and the 5R-*o*-phenanthroline (R = H, CH_3, Cl, NO_2, and C_6H_5) added to deoxygenated water together with potassium thiocyanate give rise to red precipitates having the composition $[Fe(5R\text{-}o\text{-}phen)_2(NCS)_2],xH_2O$. Chemical analyses for all the compounds give $x = 2$ (based particularly on N and H, the more reliable figures) though the possibility of the compounds being monohydrated cannot be completely ruled out. The formulation $FeL_2X_2,2H_2O$ will be used in the following discussion. The i.r. spectra of the complexes have an absorption in the vicinity of 3200—3500 cm^{-1} indicative of water. The complexes lose one molecule of water when either heated under reflux in benzene or heated in the dry state *in vacuo*. The resulting purple compounds $[Fe(5R\text{-}o\text{-}phen)_2(NCS)_2],xH_2O$ are either anhydrous ($x = 0$) or monohydrates (and the formulation FeL_2X_2,H_2O will be used in the following discussion), but definitely differ by one molecule of water

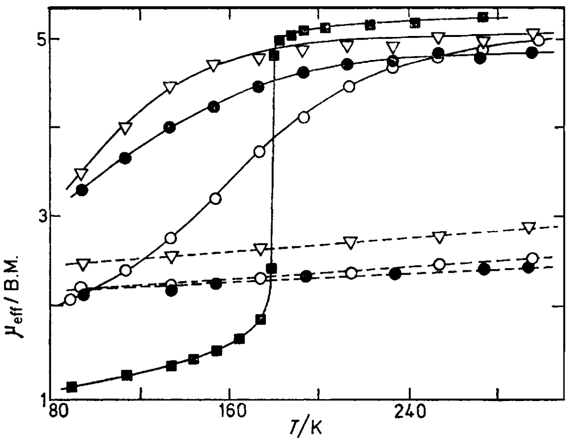

FIGURE 3 Examples of the variation of effective magnetic moment μ_{eff} with temperature for the compounds $[Fe(5R\text{-}phen)_2(NCS)_2],2H_2O$ (broken curves), and $[Fe(5R\text{-}phen)_2(NCS)_2],H_2O$ (solid curves: for ■, ○, ▽, and ●, R = H, CH_3, Cl, and NO_2 respectively (the solid curves for the three last mentioned ligands are calculated using the parameters in Table 4)

TABLE 2

Magnetic susceptibilities, $10^6\chi$/erg mol^{-1} G^{-2}, and effective magnetic moments, μ_{eff}/B.M., at various temperatures, T/K

[Fe(phen)$_2$(NCS)$_2$],2H$_2$O

T	88	113	133	193	233	273	298
$10^6\chi$	11,189	8799	6629	5399	4599	3879	3569
μ_{eff}	2·80	2·81	2·84	2·88	2·92	2·97	2·97

[Fe(5Cl-phen)$_2$(NCS)$_2$],2H$_2$O

T	93	133	173	213	253	293
$10^6\chi$	8697	6437	5227	4467	3857	3524
μ_{eff}	2·54	2·61	2·68	2·75	2·79	2·87

[Fe(5-phen)$_2$(NCS)$_2$],2H$_2$O

T	93	133	173	213	253	298
$10^6\chi$	14,826	10,526	8066	6726	5516	4876
μ_{eff}	3·32	3·34	3·34	3·38	3·34	3·40

[Fe(5NO$_2$-phen)$_2$(NCS)$_2$],2H$_2$O

T	93	113	153	193	233	273	293
$10^6\chi$	6739	5599	4329	3629	3049	2706	2599
μ_{eff}	2·23	2·24	2·30	2·36	2·38	2·43	2·46

[Fe(5Me-phen)$_2$(NCS)$_2$],2H$_2$O

T	93	133	173	213	253	295
$10^6\chi$	6821	5051	3971	3416	3061	2716
μ_{eff}	2·25	2·31	2·34	2·41	2·48	2·53

[Fe(5Cl-phen)$_2$Cl$_2$],2H$_2$O

T	90·3	118·6	151·7	195·0	222·3	265·0
$10^6\chi$	39,015	29,200	22,950	17,402	15,855	13,401
μ_{eff}	5·30	5·26	5·27	5·20	5·30	5·32
T	292·3	320·2				
$10^6\chi$	12,281	11,052				
μ_{eff}	5·35	5·31				

[Fe(Me$_4$-phen)$_2$Cl$_2$],2H$_2$O

T	95·0	119·8	167·2	223·5	288·6
$10^6\chi$	38,084	29,729	21,258	16,104	12,676
μ_{eff}	5·37	5·33	5·31	5·36	5·40

[Fe(Me$_4$-phen)$_2$(NCS)$_2$],H$_2$O

T	83·4	114·0	142·0	179·6	218·6	253·2
$10^6\chi$	45,123	33,628	25,963	20,442	16,708	14,440
μ_{eff}	5·48	5·53	5·42	5·41	5·39	5·41
T	293·2	325·2	356·5			
$10^6\chi$	12,405	11,262	10,300			
μ_{eff}	5·39	5·41	5·41			

[Fe(5Cl-phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 1)

T	93	113	133	153	173	193
$10^6\chi$	16,997	18,417	19,167	18,437	16,807	15,457
μ_{eff}	3·55	4·07	4·51	4·74	4·82	4·88
T	213	233	253	273	296	
$10^6\chi$	14,427	13,037	12,457	11,357	10,747	
μ_{eff}	4·95	4·92	5·02	4·97	5·04	

[Fe(5Cl-phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 2)

T	84·0	104·0	120·8	136·4	152·0	167·8
$10^6\chi$	6255	5986	6220	6976	8282	9747
μ_{eff}	2·04	2·23	2·45	2·75	3·15	3·61
T	182·9	190·5	200·8	215·4	233·0	247·3
$10^6\chi$	11,489	12,283	13,004	13,628	13,557	13,066
μ_{eff}	4·09	4·32	4·56	4·84	5·02	5·08
T	267·4	296·2	337·7	372·5		
$10^6\chi$	12,437	11,245	9998	9035		
μ_{eff}	5·15	5·16	5·19	5·18		

[Fe(5Me-phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 1)

T	88	113	133	153	173	193
$10^6\chi$	6481	6721	7501	8631	10,301	11,251
μ_{eff}	2·13	2·46	2·82	3·24	3·77	4·16
T	213	233	253	273	298	
$10^6\chi$	11,821	11,801	11,451	10,921	10,451	
μ_{eff}	4·48	4·68	4·81	4·88	4·99	

TABLE 2 (*Continued*)

[Fe(5Ph-phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 1)

T	93	113	133	153	173	193
$10^6\chi$	10,566	9046	8046	7316	6816	6516
μ_{eff}	2·80	2·85	2·92	2·99	3·07	3·17
T	213	233	253	273	292	
$10^6\chi$	6236	6016	5886	5836	5826	
μ_{eff}	3·25	3·34	3·45	3·56	3·68	

[Fe(5NO$_2$-phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 1)

T	93	113	133	153	173	193
$10^6\chi$	15,201	15,254	15,401	14,921	14,601	14,001
μ_{eff}	3·36	3·71	4·04	4·27	4·49	4·64
T	213	233	253	273	295	
$10^6\chi$	13,151	12,202	11,561	10,551	10,010	
μ_{eff}	4·73	4·76	4·83	4·79	4·85	

[Fe(5NO$_2$-phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 2)

T	88·6	120·0	149·3	162·1	211·0	233·1
$10^6\chi$	14,194	14,480	14,621	14,392	12,875	12,008
μ_{eff}	3·17	3·72	4·17	4·31	4·66	4·73
T	264·8	293·0	319·9			
$10^6\chi$	11,129	10,479	9620			
μ_{eff}	4·85	4·95	4·96			

[Fe(phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 1)

T	88	113	133	143	153	163
$10^6\chi$	1839	1799	1794	1859	1949	2124
μ_{eff}	1·13	1·27	1·38	1·45	1·54	1·66
T	173	178	180	183	188	193
$10^6\chi$	2567	4199	16,289	17,250	17,099	16,949
μ_{eff}	1·88	2·44	4·84	5·02	5·07	5·11
T	203	223	243	273		
$10^6\chi$	16,349	15,069	13,969	12,649		
μ_{eff}	5·15	5·18	5·21	5·25		

[Fe(phen)$_2$(NCS)$_2$],H$_2$O (Preparation method 2)

T	87·7	102·5	121·2	140·5	164·5	177·9
$10^6\chi$	2517	2372	2150	1946	1863	2177
μ_{eff}	1·32	1·40	1·44	1·47	1·56	1·75
T	181·2	184·4	185·5	188·7	191·5	197·5
$10^6\chi$	2478	7455	12,979	16,541	17,001	16,841
μ_{eff}	1·89	3·31	4·38	4·99	5·10	5·15
T	210·2	232·9	273·7	313·2	347·0	397·0
$10^6\chi$	16,034	14,737	12,493	11,027	9883	8653
μ_{eff}	5·19	5·23	5·22	5·25	5·23	5·24
T	454·0	520·0				
$10^6\chi$	7458	6498				
μ_{eff}	5·20	5·19				

[Fe(Me$_2$-bipy)$_2$(NCS)$_2$],H$_2$O Data points in order of measurement

T	88·5	120·5	179·6	234·0	300·5	263·4
$10^6\chi$	1107	744	556	658	3506	1180
μ_{eff}	0·88	0·84	0·89	1·11	2·90	1·57
T	269·2	270·4	271·3	273·7	275·8	279·2
$10^6\chi$	1279	1291	1480	1497	1736	2132
μ_{eff}	1·65	1·67	1·79	1·81	1·95	2·18
T	283·0	287·2	293·2	298·5	305·2	311·5
$10^6\chi$	2270	2532	3083	3240	3711	4569
μ_{eff}	2·26	2·41	2·68	2·78	3·00	3·37
T	320·0	328·2	334·0	343·8	357·2	371·2
$10^6\chi$	5275	6069	6897	7151	7378	8083
μ_{eff}	3·67	3·99	4·29	4·43	4·59	4·89
T	377·3	381·7	311·4	423·7	444·2	480·0
$10^6\chi$	8176	8291	8212	8114	8022	7300
μ_{eff}	4·96	5·03	5·19	5·24	5·33	5·29
T	506·7	293·0				
$10^6\chi$	7196	3013				
μ_{eff}	5·40	2·65				

[Fe(Me$_2$-bipy)$_2$(NCSe)$_2$],H$_2$O

T	79·2	122·2	170·8	222·7	267·9	299·8
$10^6\chi$	1500	1182	942	867	1411	2924
μ_{eff}	0·97	1·07	1·13	1·24	1·73	2·64
T	353·5	381·5				
$10^6\chi$	6879	7694				
μ_{eff}	4·40	4·84				

from the red compounds. This is in agreement with the work of Driver and Walker.[20] The i.r. spectra of the purple compounds do not give evidence for the presence of water.

The *d*-values for the most intense *X*-ray powder lines of the purple *o*-phen complex are 8·84m, 8·09m, 7·25m—s, 47·4s, 3·89vs, 3·32w, 3·25w, 2·72m. These agree with those reported by Baker and Bobonich.[12]

Magnetic data are given in Table 2 (Figure 3) and Mössbauer data in Table 3. The FeL_2X_2,H_2O complexes exhibit magnetic behaviour that includes (I) and (II) described above and intermediate phenomena. In general, Mössbauer spectra indicated the presence of two distinct spin states, the proportions of which differ with temperature, as expected. Where resolution permitted, both high and low spin quadrupole splitting isomer shifts were estimated. The $FeL_2X_2,2H_2O$ complexes exhibit approximately constant moments over the available temperature range and the Mössbauer spectra consist of a peak with small quadrupole splitting, indicative of a single species. The behaviour of individual complexes is discussed in detail below.

TABLE 3

Mossbauer spectra: nuclear quadrupole splitting, ΔE_Q/mm s^{-1} for complexes FeL_2X_2,nH_2O

Class (I) and (II) Complexes

FeL_2X_2,H_2O

		High spin		Low spin	
L	X	ΔE_Q(300 K)	ΔE_Q(77 K)	ΔE_Q(300 K)	ΔE_Q(77 K)
phen	NCS	2·67	*e*	*e*	0·37
5Cl-phen	NCS	2·73	3·09	*a*	0·295
5-Me-phen	NCS	2·55	*e*	*a*	0·41
5Ph-phen	NCS	*a*	*e*	*a*	0·36
$5NO_2$-phen	NCS	2·67	3·08	*a*	0·34
Me_2-bipy	NCS	2·68	*e*	*e*	0·37

Class (III) Complexes

$FeL_2X_2,2H_2O$

L	X	ΔE_Q(300 K)	ΔE_Q(77 K)	μ_{av} [b]
5Me-phen	NCS	*a*	0·21	2·39 (±0·11)
5Ph-phen	NCS	0·20 [d]	0·28 [c]	3·36 (±0·03)
$5NO_2$-phen	NCS	0·23 [d]	0·22 [c]	2·35 (±0·09)
5Cl-phen	NCS	0·18 [d]	0·25	2·71 (±0·02)

[a] Resolution low, peaks ill defined. [b] Averaged over temperature range; standard deviation in parentheses. [c] From two determinations. [d] Broad peaks, leading to an error of about 10% in ΔE_Q. [e] Absorptions absent.

$FeL_2(NCS)_2,H_2O$, L = *bipy* or *phen*.—These complexes, which have been studied previously,[5] exhibit phenomenon (II). The transition from low to high spin behaviour occurs over a very narrow temperature range and is complete within the range. No description in terms of thermal populations of nearly equienergetic spin states is expected to apply, and none has been found to be successful in such situations.[1,4] The Mössbauer data indicate a similar sharp change.[14] Magnetic measurements on the phen complex were carried out repeatedly using ascending and descending temperatures, and no hysteresis effects were observed outside of the time required for the apparatus to reach thermal equilibrium: we did not observe the time dependent magnetic susceptibility in the crossover region reported earlier.[13]

Although such sharp changes of properties are normally attributed to co-operative phenomena, *X*-ray studies [15] at different temperatures indicate only small differences in the crystal structures of the two spin forms, suggesting an intramolecular mechanism for the change. However, the *X*-ray data do indicate the expected difference in metal–ligand bond lengths between high and low spin species, which parallels the bond length changes observed in high pressure and *X*-ray studies on iron(III) complexes exhibiting phenomenon (I).[21]

FeL_2X_2,H_2O, L = Me_2–bipy, X = NCS or NCSe.—Here the magnetic properties are intermediate between phenomena (I) and (II): in contrast to the sharp transition observed in the unsubstituted complexes, the transition here is spread over *ca.* 150 K in the thiocyanate complex, yet it is much sharper than would be expected from the Boltzmann distribution required in phenomenon (I).

$Fe(Me_4\text{-phen})_2(NCS)_2,H_2O$.—This complex is pure high spin over the available temperature range. The complex may exhibit phenomenon (II) or possibly (I) at lower temperatures, but such measurements are not available at this stage.

$FeL_2(NCS)_2,H_2O$, L = 5Cl-phen, 5Me-phen, 5Ph-phen, or $5NO_2$-phen.—These complexes fall into class (I), and their magnetic properties have been described in terms of the model which has been given previously,[4,7] and into which the small corrections resulting from distortion from octahedral symmetry and configurational mixing have been incorporated.[22,23] The distortion parameters were chosen for compatibility with the Mössbauer quadrupole splittings using a treatment of the type outlined by Golding,[24] which led to values close to -600 cm^{-1} for δ in each case. The appropriate parameters have been listed in Table 4. Further refinement of the model, especially the use of an arbitrarily temperature dependent high spin–low spin separation *E*, is considered unwarranted both for reasons of experimental accuracy and for theoretical reasons which will be discussed subsequently.[23]

The 5Cl-phen complexes prepared by methods (1) and (2) show the same general behaviour but there are significant differences in the absolute magnetic moment values. This may indicate a structural difference, but it must be noted that very slight changes in molecular

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structure can have a great effect on the magnetic properties of complexes lying near the crossover.[4,15,21,25]

FeL_2Cl_2,H_2O, L = 5Cl-phen or Me_4-phen.—These complexes are high spin over the available temperature range, as expected from the known behaviour of the analogous complexes with unsubstituted phen and bipy.[5]

TABLE 4

Magnetic parameters [a] (symbols have their usual meanings) for $[Fe(5R\text{-}phen)_2(NCS)],H_2O$ complexes

R	*Q*	*E*/cm^{-1}	*P* [b]
Cl	0·15(0·12)	700	0·45
NO_2	0·4(0·35)	700	2·2
CH_3	0·1(0·07)	950(970)	1·5
C_6H_5	0·2(0·17)	1300	2·4

[a] $\lambda = -80$ cm^{-1}, $\delta = -600$ cm^{-1}; orbital reduction factor $k = 1$; parameter values for $k = 0·8$ are given in parentheses where different values are obtained. [b] Percentage of paramagnetic impurity, calculated as Fe^{2+}, having the same parameters, except that $E \sim -\infty$.

$FeL_2(NCS)_2,2H_2O$, L = phen, 5Cl-phen, 5Ph-phen, 5NO-phen, or 5Me-phen.—These complexes all exhibit moments which are intermediate between high and low spin values and which are relatively insensitive to temperature [phenomenon (III)]. The range of moments spanned by these complexes could result from mixtures containing between 18 and 38% of pure high spin species (5·3 B.M.) in an otherwise low spin (at most 1·0 B.M.[17]) complex. This proportion of high spin species is expected to be observable in the Mössbauer data, but no such absorptions were found within the limit of resolution over a wide scan range. Moreover, quadrupole splittings observed in these complexes do not correspond to either the high spin or the low spin values in the analogous complexes above which exhibit type (I) and (II) behaviour. Thus the observed magnetic moments can only be interpreted in terms of an intermediate spin ground state, as illustrated in Figure 1. The spin-only value for such a (triplet) state is 2·83 B.M., and the observed values range over the values 2·85 ± 0·5 B.M. In view of the wide range of possible arrangements of excited states above the triplet ground state, it is not surprising that the magnetic moments of the five compounds cover so wide a range. It is interesting that the compounds $[FeL_2(NCS)_2],2H_2O$ and $[FeL_2(NCS)_2],H_2O$, which differ in composition by only one water molecule, have such different magnetic properties.

Analogous complexes, $Fe(phen)_2A,nH_2O$, which are also considered to have a triplet ground state, have quite similar Mössbauer spectra ($\Delta E_Q = 0·2$ mm s^{-1}) but significantly greater magnetic moments ($\mu_{eff} = 3·98$, 3·80 when A = oxalate or malonate respectively) than the above five complexes.[11] For the moments to be rationalised on the basis of a mixture, the $Fe(phen)_2A,nH_2O$ complexes would require 50—54% of high spin species in a low spin medium, and no evidence of this is reported in a Mössbauer study of the compounds.[11] These complexes are therefore expected to belong to the same class as the thiocyanato-complexes, the higher magnetic moments probably being associated with a different order of some of the low-lying excited states. Due to the similarity of the Mössbauer spectra, we consider it likely that the two groups of complexes have the same triplet ground state ($^3A_2$, or possibly ^3E), but there is a possibility of different ground states with fortuitously the same quadrupole splitting.

Differential Thermal Analysis.—The two complexes $[Fe(phen)_2(NCS)_2],H_2O$ and $[Fe(5Me\text{-}phen)_2(NCS)_2],H_2O$ were studied by means of qualitative differential thermal analysis over the temperature ranges 233—153 and 293—93 K respectively (Figure 2). $[Fe(phen)_2(NCS)_2],H_2O$ undergoes a rapid exothermic change as the sample temperature decreased through the temperature range for the sharp magnetic crossover. For sample temperature increasing through this range an endothermic effect was observed, and in both cases the maximum in the DTA curve is at 173 K. These results are consistent with a phase (lattice) change [13,14] or a sudden change in *Dq* resulting from an intramolecular rearrangement [15] occurring at (and promoting) the magnetic crossover. The pressure dependence of the magnetic susceptibility [21] and Mössbauer spectrum [26] of this complex also suggest this.

In contrast, $[Fe(5Me\text{-}phen)_2(NCS)_2],H_2O$ displayed DTA curves which were similar for sample heating and cooling. The DTA curves were broad, spanning the wide temperature range of the magnetic crossover and with maxima near the temperature for maximum $\Delta(\mu_{eff})/\Delta(T)$. Each DTA curve is consistent with an exothermic (or endothermic) change followed by an endothermic (or exothermic) change occurring as the temperature varies through the crossover region. As for $[Fe(phen)_2(NCS)_2],H_2O$, the susceptibility in this region is time independent.

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