

Spin Equilibria in Some New *cis*-Diisothiocyanato Iron(II) Complexes with Tetradentate Ligands of the Tris(2-pyridylmethyl)amine Type

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The preparation of five new *cis*-[FeL(NCS)₂] complexes, where L is modified tetradentate ligands of the tris(2-pyridylmethyl)amine (tpa) type, is described.

Magnetic susceptibility measurements over the temperature range 80–300 K and infrared spectra at 77 and 300 K are reported.

The results show that two of the complexes exist in a temperature-dependent high-spin ⁵T₂ ⇌ low-spin ¹A₁ equilibrium. Two of the complexes show an intermediate spin state with a temperature independent magnetic moment. One complex is a pure high-spin ⁵T₂ complex at all temperatures.

The temperature-induced low-spin ¹A₁ (Oh) ⇌ high-spin ⁵T₂ (Oh) transitions in iron(II) complexes of the type *cis*-[FeL₂(NCS)₂], where L are bidentate ligands as 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen), have been extensively studied by several techniques as described in a recent review by Gülich.¹ Some systems with modified phen or bipy ligands have been described^{1,2} as well as a series of complexes where L is Schiff-base ligands.³ All the previously investigated systems showing the spin-cross-over phenomenon contained four amine ligands of the conjugated diimine type. Recently it has been shown that iron(II) complexes of the hexadentate ligands of the tetrakis(2-pyridylmethyl)ethylenediamine (tpen) type are either low-spin or cross-over systems,⁴ suggesting that the chelate effect may be as important as the conjugation in the ligand for the formation of cross-over iron(II) systems.

In order to investigate further some of the factors which can make a ligand capable of forming a spin-cross-over iron(II) complex we decided to make a systematic investigation on some new complexes of the *cis*-[FeL(NCS)₂] type (L is various tetradentate ligands of the tris(2-pyridylmethyl)amine (tpa) type). A large variation in magnetic behaviour turned out to be represented by these systems. Two new spin-cross-over systems were found for iron (II) complexes of L=tpa and (1-(2-pyridyl)ethyl)-bis(2-pyridylmethyl)amine (L(II)), whereas with L=(6-methyl-2-pyridylmethyl)-bis(2-pyridylmethyl)amine (L(IV)) a complex which is high-spin in the whole temperature range is formed. Two complexes with a temperature-constant intermediate spin, triplet (³T₁(Oh)) or a mixture of singlet and quintet, were found for L=(2-(2-pyridyl)ethyl)-bis(2-pyridylmethyl)amine (L(III)) and bis(2-pyridylmethyl)amine (dpa) plus pyridine (py).

The spin states of the various iron(II) complexes were characterized by the variation of their magnetic susceptibility and their infrared spectra with the temperature.

EXPERIMENTAL

Instruments. Magnetic susceptibilities were measured by the Faraday method, using Hg [Co(SCN)₄] as calibrant. The equipment employs an electromagnet (Bruker-Physik), an electrical microbalance (Sartorius type 411) and a temperature unit (BVT-1000). Sample temperatures were measured using a chromel-alumel thermocouple.

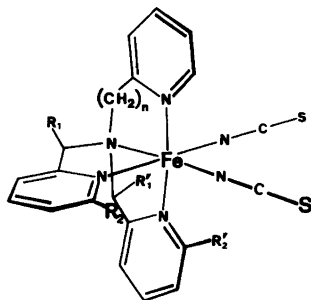


Fig. 1. Drawing of the *cis*-diisothiocyanato-tris(2-pyridylmethyl)amine iron(II) framework. The combination of substituents in the complexes used is given in Table 1.

Table 1. Combination of substituents.

R_1 or R'_1	R_2 or R'_2	Complex
$n=1$		
H	H	$[\text{Fe}(\text{tpa})(\text{NCS})_2]$
CH_3	H	$[\text{FeL}(\text{II})(\text{NCS})_2]$
H	CH_3	$[\text{FeL}(\text{IV})(\text{NCS})_2]$
$n=2$		
H	H	$[\text{FeL}(\text{III})(\text{NCS})_2]$
$n=0$		
H	H	$[\text{Fe}(\text{dpa})(\text{py})(\text{NCS})_2]$

The molar susceptibilities were corrected for ligand diamagnetism by Pascal's constants.¹⁸ The infrared spectra were obtained on a Perkin-Elmer 580 spectrometer calibrated with polystyrene. The samples were grounded in nujol and measured between KBr-plates. The low-temperature spectra were obtained with the samples placed *in vacuo* on a cold finger cooled with liquid nitrogen.

Preparation of ligands. *Tris* (2-pyridylmethyl)amine (*tpa*). This ligand was prepared by a method which was a slight modification of Andereg's method.⁵ A solution of 2-pyridylmethyl chloride hydrochloride prepared from α -picoline¹⁹ (23.6 g, 144 mmol) in water (10 ml) was neutralized with a sodium hydroxide solution (29 ml, 5 M) and 2-pyridylmethylamine (Aldrich) (7.8 g, 72 mmol) was added. During the following days a sodium hydroxide solution (29 ml, 5 M) was added with stirring in so small portions that pH never exceeded 9. The resulting dark red solution

was extracted with chloroform (3 times 150 ml). The combined extracts were dried (sodium sulfate) and the chloroform was removed on a rotary evaporator. The residue was purified by (short distance) high-vacuum distillation. The product was a yellow viscous oil, 4.2 g (35 %), b.p. 144–146 °C/0.01 mmHg.

1-(2-Pyridyl)ethyl-bis(2-pyridylmethyl)amine (*L*(II)). 2-Acetylpyridine (Aldrich) (9.3 g, 77 mmol) was dissolved in abs. ethanol (50 ml) and 2-aminomethylpyridine (Aldrich) (8.3 g, 77 mmol) was added and the solution was refluxed for 1 h. A viscous yellow oil remained after removal of solvent. It was dissolved in methanol (50 ml) and sodium tetrahydridoborate (Fluka) (1.6 g, 42 mmol) was added in small portions with stirring. The solution was left overnight. Hydrochloric acid (5 ml, 12 M) was added to the solution and when the gas evolution had ceased the solution was made alkaline with a sodium hydroxide solution (6 ml, 5 M). The solvent was evaporated *in vacuo* and water (20 ml) was added. A precipitate of sodium borate was filtered off. To the filtrate, 2-pyridylmethyl chloride hydrochloride (12.6 g, 77 mmol) was added and a sodium hydroxide solution (15 ml, 5 M) was added. During the following days sodium hydroxide solution (15 ml, 5 M) was added with stirring in such small portions that pH never exceeded 9. The resulting dark red solution was extracted with chloroform (3 times 100 ml). The combined extracts were dried (sodium sulfate) and the solvent was removed. The residue was purified by high vacuum distillation. The product was a yellow viscous oil, 2.3 g (10 %) b.p. 149–152 °C/0.01 mmHg.

2-(2-Pyridyl)ethyl-bis(2-pyridylmethyl)amine (*L*(III)). This ligand was prepared by the same method as used for *tpa*. 2-(2-Pyridyl)ethylamine (Aldrich) (9.8 g, 80 mmol) was treated with 2-pyridylmethyl chloride hydrochloride (30 g, 183 mmol) and sodium hydroxide (73 ml, 5 M). Purification by distillation gave a yellow viscous oil, 2.3 g (10 %), b.p. 154–256 °C/0.01 mmHg.

Bis(2-pyridylmethyl)amine (*dpa*). To a solution of 2-aminomethylpyridine (Aldrich) (10 g, 92 mmol) in abs. ethanol (20 ml) was added 2-pyridinecarbaldehyde (Aldrich) (10 g, 93 mmol). The solution was refluxed for 10 min. The solvent was removed and the residue dissolved in methanol (50 ml). Sodium tetrahydridoborate (Fluka) (1.9 g, 50 mmol) was added in small portions with stirring and the solution was left overnight. Excess of sodium tetrahydroborate was destroyed with hydrochloric acid (5 ml, 12 M). After removing the solvent and dissolving the residue in water (10 ml), the solution was made alkaline with a sodium hydroxide solution (7 ml,

5 M).

A precipitate of sodium borate was filtered off and the solution extracted with chloroform (3 times 100 ml). The combined extracts were dried (sodium sulfate) and the solvent was removed. The residue was distilled as above. The product was a pale yellow viscous oil, 2 g (21 %), b.p. 145 °C/0.2 mmHg.

(6-Methyl-2-pyridylmethyl)-bis(2-pyridylmethyl)amine (L(IV)). This ligand was prepared by the same method as used for tpa. Dpa, prepared as described above, (9.5 g, 48 mmol) was treated with 6-methyl-2-pyridylmethyl chloride hydrochloride, prepared from 2,6-lutidine and sodium hydroxide (19 ml, 5 M). The product was a pale yellow viscous oil, 2 g (14 %), b.p. 154–156 °C/0.01 mmHg.

Preparation of complexes. All iron(II) complexes were prepared under nitrogen in N₂-saturated solvents. *trans*-Diisothiocyanatotetrapyridineiron(II), prepared as described in the literature,¹⁹ was dissolved in boiling abs. ethanol (10 ml) and the ligand (2 mmol) dissolved in boiling abs. ethanol (5 ml) was added with stirring. The solution was slowly cooled to room temperature. The precipitated iron(II) complex was filtered off and washed with abs. ethanol and dried over sulphuric acid. The yields were in all cases about 3 g (65 %). (Anal. C,H,N,S).

RESULTS AND DISCUSSION

Preparations. The tetradentate ligands tris(2-pyridylmethyl)amine (tpa) and (2-(2-pyridyl)ethyl)-bis(2-pyridylmethyl)amine [L(III)] were prepared by reacting 2-pyridylmethylamine or [2-(2-pyridyl)ethyl]amine with 2-pyridylmethyl chloride which is a modification of the method used by Anderegg for the preparation of tpa.⁵ The ligand (6-methyl-2-pyridylmethyl)-bis(2-pyridylmethyl)amine [L(IV)] was prepared by reaction between bis(2-pyridylmethyl)amine and 6-methyl-2-pyridylmethyl chloride. [1-(2-Pyridyl)ethyl]-bis(2-pyridylmethyl)amine [L(II)] was prepared *via* the Schiff-base of 2-acetylpyridine and 2-pyridylmethylamine by reduction with sodium tetrahydridoborate. The remaining 2-pyridylmethyl group was introduced with 2-pyridylmethylchloride as above.

The bis-isothiocyanato iron(II) complexes were all prepared in a nitrogen atmosphere by reacting *trans*-[FePy₄(NCS)₂] with the respective ligands in boiling absolute ethanol. The analytical data show good agreement between found and calculated values for all the metal complexes.

All the bis-isothiocyanato iron(II) complexes with the tetradentate ligands seem to be stable and resist air oxidation in the solid state at room temperature. Thus they show no change in coloration or IR spectra by storing for months.

The colour of the complexes varies from bright yellow for *cis*-[FeL(IV)(NCS)₂] to red brown for *cis*-[FeL(II)(NCS)₂]. *cis*-[Fe(tpa)(NCS)₂] and *cis*-[FeL(II)(NCS)₂] shows a very striking change in coloration on cooling from room temperature to liquid nitrogen temperature going from yellow to deep red.

Magnetic measurements. The magnetic measurements were made on solid samples in the temperature range 77 or 100 K to 300 or 350 K. All measurements were made at three different field strengths and no field dependence was observed. The data were recorded with ascending temperature. The compounds showed signs of decomposition at temperature above 350 K.

The temperature dependence of the effective magnetic moments μ_{eff} of the five iron(II) complexes are shown in Fig. 2. The highest and lowest μ_{eff} for each compound in this work as well as some relevant compounds from the literature are shown in Table 2.

cis-[FeL(IV)(NCS)₂] exhibits a behaviour typical for a high-spin pseudo-octahedral iron(II) complex (ground state ⁵T₂), with a nearly constant magnetic moment of 5.25–5.40 BM in the temperature range 77–300 K. However, strongly temperature dependent magnetic moments were observed for *cis*-[Fe(tpa)(NCS)₂] and *cis*-[FeL(II)(NCS)₂], changing from about 2.9 to 5.4 BM in the temperature range 80–300 K.

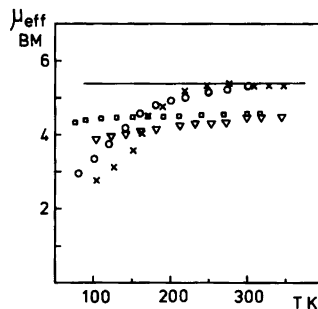


Fig. 2. The temperature dependence of the effective magnetic moment μ_{eff} BM. —, *cis*-[FeL(IV)(NCS)₂]; ×, *cis*-[Fe(tpa)(NCS)₂]; O, *cis*-[FeL(II)(NCS)₂]; □, *cis*-[FeL(III)(NCS)₂]; ∇, *cis*-[Fe(dpa)(py)(NCS)₂].

Table 2. Effective magnetic moment at liquid nitrogen temperature and at room temperature.

Compound	μ_{eff} BM at 80 K	μ_{eff} BM at 300 K	Ground state	Ref.
[FeL(IV)(NCS) ₂]	5.25	5.40	5T_2	This work
[Fe(2-CH ₃ phen) ₂ (NCS) ₂]	5.37	5.42	5T_2	17
[Fe(tpa)(NCS) ₂]	2.83	5.46	$^5T_2 \rightleftharpoons ^1A_1$	This work
[FeL(II)(NCS) ₂]	2.94	5.33	$^5T_2 \rightleftharpoons ^1A_1$	
[Fe(phen) ₂ (NCS) ₂]	0.71	5.17	$^5T_2 \rightleftharpoons ^1A_1$	8
[FeL(III)(NCS) ₂]	4.33	4.59	$^5T_2 + ^3T_1$	This work
[Fe{4,7(C ₆ H ₅) ₂ (phen)} ₂ (NCS) ₂]	4.13	4.28 ^a	$^5T_2 + ^3T_1$	3
[Fe(dpa)(py)(NCS) ₂]	3.88 ^b	4.50	$^5T_2, ^3T_1, ^1A_1$	This work

^a Value corresponding to 352 K. ^b Value corresponding to 100 K.

In contrast to *cis*-[Fe(phen)₂(NCS)₂] the spin changes are gradual and the residual paramagnetic moments at low temperature are relatively high. The residual magnetic moment presumably depends on the method of preparation. Thus, in the case of *cis*-[Fe(tpa)(NCS)₂], a sample of relatively large crystals precipitated from a pyridine solution shows a moment of 2.83 BM at 100 K whereas a sample of smaller crystals precipitated from absolute ethanol gave 3.76 BM at 100 K. Both samples crystallize without crystal solvent so the variation probably reflects some differences in the size of the domains in the crystals.⁶

The magnetic moment of *cis*-[FeL(III)(NCS)₂] changes only very slightly with the temperature, suggesting no spin change for this compound, but the effective magnetic moment is only 4.52 BM corresponding to 65 % of a pure high-spin phase 5T_2 mixed with 35 % of a pure low-spin phase 1A_1 or a mixture of equal amounts of a triplet phase 3T_1 and a quintet phase 5T_2 . *cis*-[Fe(4,7(C₆H₅)₂phen)₂(NCS)₂] exhibits a very similar magnetic behaviour.³ In this case a mixture of equal amounts of triplet and quintet is suggested.

The mixed ligand complex *cis*-[Fe(dpa)py(NCS)₂] also has a reduced magnetic moment at room temperature which gradually decreases to 3.88 at 77.

Infrared measurements. In order to have a microscopic criterium to supplement the macroscopic magnetic susceptibility information, we have measured the infrared spectrum at room temperature and at liquid nitrogen temperature in the region 4000–250 cm⁻¹ for all the com-

plexes. The region of the C–N stretching frequency of NCS is particularly useful in characterizing the ground state. It has been demonstrated that a 5T_2 ground state normally shows a strong doublet at 2060–2080 cm⁻¹ whereas another strong doublet characteristic of a 1A_1 ground state appears at 2100–2120 cm⁻¹.^{7,8} Fig. 3 shows the temperature variation of the IR spectrum of *cis*-[Fe(tpa)(NCS)₂] which is typical. It appears that each doublet is further split up presumably due to the fact that the two NCS groups are in different environments. The low-temperature spectrum shows lines both in the 2060–2080 cm⁻¹ region and in the 2100–2120 cm⁻¹ region. Therefore, we can conclude that the present transitions are characterized by the coexistence of the high-spin and low-spin ground state around and below the transition temperature T_c , ruling out any antiferromagnetic binuclear structure or any kind of admixed spin states. The frequencies for

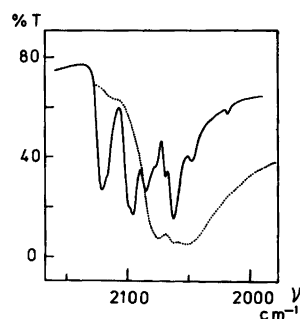


Fig. 3. The infrared spectra of *cis*-[Fe(tpa)(NCS)₂] in the CN stretching region. ···, Recorded at 300 K; —, recorded at 77 K.

Table 3. Infrared stretching frequencies in the C–N and in the Fe–N region.

Compound	$\nu_{\text{CN}} \text{ cm}^{-1}$ at 77 K			$\nu_{\text{FeN}} \text{ cm}^{-1}$ at 77 K	$\nu_{\text{CN}} \text{ cm}^{-1}$ at 300 K			$\nu_{\text{FeN}} \text{ cm}^{-1}$ at 300 K		
	1A_1	3T_1	5T_2		1A_1	3T_1	5T_2			
[FeL(IV)(NCS) ₂]			2078	2067	483		2073	2060	483	
[Fe(tpa)(NCS) ₂]	2122	2095	2086	2062	532	480	2074	2060	479	
[FeL(II)(NCS) ₂]	2108	2091	2081	2051	490	480	2074	2057	(534)	
[FeL(III)(NCS) ₂]		2101	2086	2081	528	483	2096	2082	2077	524
				2062						480
[Fe(dpa)(py)(NCS) ₂]	2118	2099	2080	2059	530	482	2095	2076	2055	526
										480

all the systems are shown in Table 3. In this table the low-spin Fe–NCS stretching frequencies are also shown. The corresponding high-spin frequencies are expected to appear at 250 cm^{-1} outside the detection region of our spectrometer.

cis-[FeL(IV)(NCS)₂] is clearly pure high-spin in the whole temperature range.

cis-[Fe(tpa)(NCS)₂], *cis*-[FeL(II)(NCS)₂] and *cis*-[Fe(dpa)py(NCS)₂] are seen to be spin-cross-over systems also according to the IR criterium. *cis*-[FeL(III)(NCS)₂], however, does not show any temperature dependence in the IR spectrum. In this case a constant 2:1 ratio of high-spin 5T_2 and low-spin 1A_1 species or a 1:1 ratio of 5T_2 and 3T_1 are in accordance with the position of the lines, but the equal intensity of the two sets of lines favours the last possibility. Thus a high-spin low-spin equilibrium does not occur here.

cis-[Fe(dpa)py(NCS)₂] also seems to contain approximately 30 % of a permanent low spin or intermediate spin component.

The increase in the C–N stretching frequencies of the NCS[−] ligand in the spin-cross-over system by 30–40 cm^{-1} when going from high-spin to low-spin is a little less than the 40–50 cm^{-1} observed for other similar systems,⁸ whereas the intermediate spin systems are only shifted by 20–30 cm^{-1} compared to the high-spin systems. König and Madeja⁹ explain the increase in the ν_{NC} as an increase of the Fe–NCS bond due to a decrease in π -acceptor ability of NCS[−] on going from high-spin to low-spin. However the isothiocyanate ion is not considered to be a good π -acceptor, the ligand field strength is even less than for ammonia so the increase in the ν_{NC} must be explained as mainly due to an increase in the σ -donation when going from high-spin to low-

spin. According to the MO scheme of NCS[−]¹⁰ the lone pair on N is slightly antibonding, so a σ -donation results in a net increase in the bond-order of the C–N bond, explaining the increase in the ν_{CN} . Madeja has suggested that the ν_{CN} of a diisothiocyanato iron(II) complex with a triplet ground state should be approximately 2050 cm^{-1} .^{3,20} However, the true triplet nature of the complexes his measurements are made on, has been questioned.¹ If we assume that the ν_{NC} of a triplet ground-state iron(II) complex ($t_{2g}^5 e_g$) is the mean value of a high-spin case ($t_{2g}^4 e_g^2$) and a low-spin case (t_{2g}^6) a value of 2095–2085 cm^{-1} is suggested which is not far from the values found for *cis*-[FeL(III)(NCS)₂] (2101, 2086 cm^{-1}) and *cis*-[Fe(dpa)py(NCS)₂] (2099, 2087 cm^{-1}). As the occupancy of the e_g orbitals are expected to be crucial for the strength of the Fe–N bond the assignment given above is chemically reasonable.

Inspection of the Tanabe-Sugano diagrams for the d^6 configuration shows that at the cross-over point of 5T_2 and 1A_1 the lowest triplet state 3T_1 is not far above the ground state. A lowering of the symmetry will cause the 3T_1 state to split and a stabilization of a triplet state 3A_2 might be sufficient to make this the ground-state. König and Kremer have shown that with a tetragonal distortion, corresponding to $Dt=1000 \text{ cm}^{-1}$, all three states can coexist for a rather large range of Dq values.¹¹ Cross-over behaviour involving triplet states has very rarely been observed (if ever) in iron(II) complexes so far,¹² but some [FeL₂X₂] complexes, where L are diimines and X=Cl[−], Br[−], NCS[−], N₃[−], and $1/2$ mal (= half a molecule of malonate) are reported to have triplet ground states.^{3,12,16} Recently, however, König has shown

that e.g. the mal complex has the composition $[\text{Fe}^{\text{II}}(\text{phen})_3]_2[\text{Fe}^{\text{III}}(\text{mal})_3]^{1/2}(\text{mal})(\text{aq})$.²¹

Comparison of the systems. In the following we shall try to rationalize the various magnetical behaviour arising from chemical (steric and inductive) effects. We realize that the solid state effects (domain size) can be important, thus all the complexes discussed in this section are prepared under the same conditions.

Fig. 1 shows the various modifications of the ligand system dealt with in this work. The parent compound *cis*- $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ is, from the IR spectra, seen to possess a D_{2h} symmetry based on the octahedron and not a trigonal bipyramidal structure. The same is assumed to be the case for all the complexes in this work.

That the tpa complex is a spin-cross-over system like the bipy and phen complexes despite the fact that no conjugated diimine functions are present in the tpa ligand suggests that the additional chelate-ring in tpa, compared to two bipy or phen ligands, has compensated for the expected decrease in π -acceptor ability.

In the complex *cis*- $[\text{FeL}(\text{IV})(\text{NCS})_2]$ (R_2 or $\text{R}'_2 = \text{CH}_3$) where a methyl group is substituted in the 6-position of one of the pyridine rings, two geometrical isomers are possible. If the product is a mixture of these isomers both must be pure high-spin forms within the temperature range used. The high-spin nature of this complex is probably due to *intra*-molecular non-bonding interactions between the 6-methyl group and one of the isothiocyanate groups, resulting in an increase of the Fe-N distances and a reduction in the ligand field strength. The same argument has been used to explain that *cis*- $[\text{Fe}(2\text{-Meph})_2(\text{NCS})_2]$ is a high-spin complex.¹³ CH_3 has a stronger σ -donation power than hydrogen increasing the basicity of the nitrogen atom and making the Fe-N σ -bond somewhat stronger. This electronic effect is seen to be more than counterbalanced by the steric effect in the L(IV) case. However if the CH_3 group is substituted in one of the methylene groups as in L(II) (R_1 or $\text{R}'_1 = \text{CH}_3$) no steric interactions are present in the complexes and the electronic effect is expected *a priori* to dominate. Nevertheless, *cis*- $[\text{FeL}(\text{II})(\text{NCS})_2]$ has a spin transition which is very similar to that for the corresponding tpa complex. This effect might be explained within the framework of the theory that the methylene group in the 2-pyridylmethyl amine chelate ring

mediates an electronic conjugation in this ring.¹⁴ Substituting H for CH_3 in the chelate ring is expected to break the conjugation resulting in a decrease in the π -acceptor ability. *cis*- $[\text{FeL}(\text{II})(\text{NCS})_2]$ can exist in 3 enantiomeric pairs due to a regio isomerism of the two CH_3 groups (R, or $\text{R}' = \text{CH}_3$). The product presumably is a mixture of these isomers.¹

Expansion of one chelate ring from five-membered to six-membered (tpa vs. L(III)) is expected also to result in a decrease in the ligand field. On the other hand, the fusion of two five-membered chelate rings in a meridional plane is known to give rise to enough strain to distort the ligand field so much that the high-spin state will be favoured.⁴ Meridional strain is probably also the explanation for the fact that only the facial isomers are formed when preparing the chromium(III) complexes of bis(2-pyridylmethyl)ethylenediamine.¹⁵ The meridional strain is released if one six-membered ring is fused in a meridional fashion to one of the five-membered rings. Such a structure as the one indicated in Fig. 1 ($n=2$) is expected for *cis*- $[\text{FeL}(\text{III})(\text{NCS})_2]$ and the structure of *cis*- $[\text{Fe}(\text{dpa})\text{py}(\text{NCS})_2]$ will possess the same facial structure [corresponding to a removal of (CH_2)]. As explained earlier, these two complexes are characterized by having a permanent low-spin or intermediate spin component. Whether this behaviour is due to a coexistence of all three ground states in one geometrical isomer or if it is because the sample is a mixture of different geometrical isomers having different ground states is not possible to decide from the present data. But, as pointed out above, only one isomer is expected to be formed for each compound.

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