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

HANS TOFTLUND,[a] ERIK PEDERSEN[b] and STEEN YDE-ANDERSEN[a]

[a] Department of Chemistry, University of Odense, DK-5230 Odense M, Denmark and
[b] Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark

The preparation of five new *cis*-[FeL(NCS)$_2$] complexes, where L are modified tetradentate ligands of the bis(2-pyridylmethyl)-diamine type, is described.

Magnetic susceptibility measurements over the temperature range 4–300 K and infrared spectra at 300 K are reported.

The results show that two of the complexes exist in a temperature-dependent high-spin $^5T_2 \rightleftarrows$ low-spin $^1A_1$ equilibrium. The remaining three complexes are high-spin $^5T_2$ complexes at all temperatures.

The temperature-induced low-spin $^1A_1$ $(O_h) \rightleftarrows$ high-spin $^5T_2$ (O_h) transitions in iron(II) complexes of the type *cis*-[FeL$_2$ (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 Gütlich.[1] Some systems with modified phen or bipy ligands have been described[1,2] as well as a series of complexes where L are Schiff-base ligands.[3] Recently it has been shown that iron(II) complexes of the tetradentate ligands of the tris(2-pyridylmethyl)-amine (tpa) are either high-spin or crossover systems,[4] suggesting that the chelate effect may be as important as the conjugation in the ligand for the formation of crossover iron(II) systems.

In order to investigate further some of the factors which can make a ligand capable of forming a spin-crossover iron(II) complex, we decided to make a systematic investigation on some new complexes of the type *cis*-[FeL(NCS)$_2$] where L are various tetradentate ligands of the bis(2-pyridylmethyl)diamine type. Two new spin-crossover systems were found for iron(II)-complexes with *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine [bispicen = L(I)] and with *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine [bispictn = L(II)]. Complexes with the ligands *N*-(6-methyl-2-pyridylmethyl)-*N'*-(2-pyridylmethyl)-1,2-ethanediamine [L(III)], *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine [L(IV)], and *N,N'*-bis(6-methyl-2-pyridylmethyl)-1,2-ethanediamine [L(V)] exhibit high-spin in the whole temperature range.

The spin states of the various iron(II) complexes were characterized by the variation of the magnetic susceptibility with the temperature in the range 4–300 K.

RESULTS AND DISCUSSION

Preparations. The tetradentate ligand [L(IV)] was prepared by reacting *N,N'*-dimethyl-1,2-ethanediamine with 2-pyridylmethyl chloride, which is a modification of the method used by Anderegg for the preparation of tpa.[5] The remaining four ligands [L(I), L(II), L(III), L(V)] were prepared via the Schiff-bases of 2-pyridinecarbaldehyde or 6-methyl-2-pyridinecarbaldehyde and a diamine by reduction with sodium tetrahydridoborate as described previously.[6] All the tetradentate ligands were purified by short-

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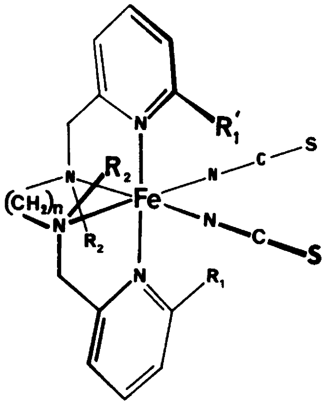

Fig. 1. Drawing of the *cis*-diisothiocyanato bis(2-pyridylmethyl)diamine iron(II) framework. The combination of substituents in the complexes used is given in the table:

R_1	R'_1	R_2	Complex
n=2			
H	H	H	*cis*-[Fe L(I)(NCS)$_2$]
CH_3	H	H	*cis*-[Fe L(III)(NCS)$_2$]
CH_3	CH_3	H	*cis*-[Fe L(V)(NCS)$_2$]
H	H	CH_3	*cis*-[Fe L(IV)(NCS)$_2$]
n=3			
H	H	H	*cis*-[Fe L(II)(NCS)$_2$]

distance high-vacuum distillation.

The bis-isothiocyanato iron(II) complexes were all prepared in a nitrogen atmosphere by reacting iron(II) thiocyanate in water with the respective ligands in ethanol.

The analytical data (C,H,N,S) show good agreement between found and calculated values for all the metal complexes.

All the complexes seem to be stable and resist air oxidation in the solid state at room temperature. Thus they show no change in colour or IR spectra by storing for months.

The colour of the complexes varies from bright yellow for *cis*-[FeL(IV)(NCS)$_2$] to green for *cis*-[FeL(II)(NCS)$_2$]. *cis*-[FeL(I)(NCS)$_2$] and *cis*-[FeL(II)(NCS)$_2$] show a very striking change on cooling from room temperature to liquid nitrogen temperature turning from yellow to deep red and from green to dark redish brown, respectively.

Magnetic measurements. The magnetic measurements were made on solid samples in the temperature range 4 K to 300 K. The data were recorded with ascending temperature. In the cases of *cis*-[FeL(I)(NCS)$_2$] and *cis*-[FeL(II)(NCS)$_2$], measurements with decreasing temperature were performed as well.

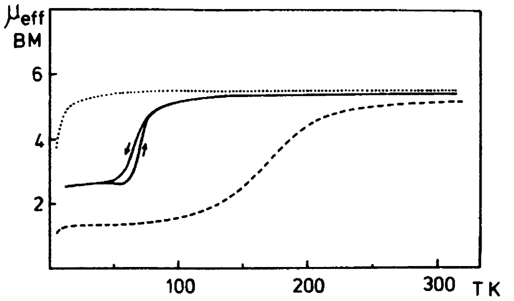

Fig. 2. The temperature dependence of the effective magnetic moment μ_{eff} BM ..., *cis*-[Fe L(V)(NCS)$_2$];—, *cis*-[FeL(I)(NCS)$_2$]; – – –, *cis*-[FeL(II) (NCS)$_2$]. Each curve consist of several hundred points. The scatter does not exceed the line thickness in the drawing.

The temperature dependence of the effective magnetic moments μ_{eff} of three 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 1.

cis-[FeL(III)(NCS)$_2$] and *cis*-[FeL(V)(NCS)$_2$] exhibit a behaviour typical for a high-spin pseudo-octahedral iron(II) complex (ground state $^5T_2$), with a nearly constant magnetic moment of 5.5 BM in the temperature range 70–300 K. The drop of the magnetic moments at low temperatures can be interpreted as the consequence of intermolecular exchange. *cis*-[FeL(IV)(NCS)$_2$] as well was high-spin, but with a magnetic moment of 5.06 BM. Strongly temperature dependent magnetic moments were observed for *cis*-[FeL(I)(NCS)$_2$] and *cis*-[FeL(II)(NCS)$_2$], however, changing from 2.4 to 5.4 BM in the temperature range 40–100 K and from 1.4 to 5.2 BM in the temperature range 50–300 K, respectively.

cis-[FeL(I)(NCS)$_2$] revealed one of the lowest transition temperatures yet seen for this kind of complexes (T_c~70 K). The temperature variation of the magnetic moment with decreasing temperature is reproducible only if cooling from 100 to 4 K is performed during several hours. With increasing temperature the variation is reproducible and rate independent ($\Delta T/\Delta t$<10 mK s^{-1})

Table 1. Effective magnetic moment at liquid nitrogen temperature and at room temperature.

Complex	μ_{eff}BM at 77 K	μ_{eff}BM at 300 K	Ground state	Ref.
[Fe L(V)(NCS)$_2$]	5.45	5.53	$^5T_2$	This work
[Fe L(III)(NCS)$_2$]	5.42	5.58	$^5T_2$	–
[Fe L(IV)(NCS)$_2$]	5.00	5.06	$^5T_2$	This work
[Fe(2-CH$_3$phen)$_2$(NCS)$_2$]	5.37	5.42	$^5T_2$	13
[Fe(2,9-(CH$_3$)$_2$-phen)$_2$(NCS)$_2$]	4.76	4.80	$^5T_2$	14
[Fe L(I)(NCS)$_2$]	2.35[a]	5.42	$^5T_2 \rightleftarrows {}^1A_1$	This work
[Fe L(II)(NCS)$_2$]	1.38[a]	5.18	$^5T_2 \rightleftarrows {}^1A_1$	-
[Fe (tpa)(NCS)$_2$]	2.83	5.46	$^5T_2 \rightleftarrows {}^1A_1$	4
[Fe(phen)$_2$(NCS)$_2$]	0.71	5.17	$^5T_2 \rightleftarrows {}^1A_1$	8

[a] Value corresponding to 50 K.

provided the original cooling was very slow. If the sample is cooled rapidly from room temperature to 4 K it can be frozen in a state of almost high spin with μ_{eff}~4. During subsequent increase of the temperature the moment first increases to about 4.5 BM then from ca. 50 K drops to a minimum of 3 BM at 60 K, and finally it follows the regular variation. Spin equilibration is, therefore, very slow below 60 K. Even for an extremely slow cyclus a hysteresis curve is obtained as shown in Fig. 2. The width of the hysteresis curve is more than 4 K which is much higher than seen for *cis*-[Fe(phen)$_2$(NCS)$_2$].[7] Although the ascending curve of the L(I) complex is relatively steep it is far from as abrupt as the corresponding curve of the phen complex.[7] In the case of *cis*-[FeL(II)(NCS)$_2$] the transition temperature T_c is 170 K and the transition is gradual, extending over two hundred degrees. There is no indication of hysteriesis in this case. Both the spin-equilibrium systems exhibit a residual paramagnetic moment at low temperatures although it is not as large as seen for *cis*-[Fe(tpa)(NCS)$_2$].[4]

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 2500–2000 cm^{-1} for *cis*-[FeL(I)(NCS)$_2$]. The region of the C–N stretching frequency of NCS is particularly useful in characterizing the ground state. It has been demonstrated that *cis*-complexes with a $^5T_2$ ground state normally show a strong doublet at 2060–2080 cm^{-1}, whereas another strong doublet characteristic of an $^1A_1$ ground state appears at 2100–2120 cm^{-1}.[4,8,9] High-spin complexes with a *trans* configuration, such as *trans*-[Fe py$_4$(NCS)$_2$], show a single intense line at about 2065 cm^{-1}. All the complexes in the present work show a doublet in the 2060 to 2080 region at room temperature. Fig. 3 shows the temperature variation of the IR spectrum of *cis*-[FeL(I)(NCS)$_2$]. The fact that each doublet is not further split up, suggest a symmetric structure for this complex in contrast to *cis*-[Fe(tpa)(NCS)$_2$].[4] The low-

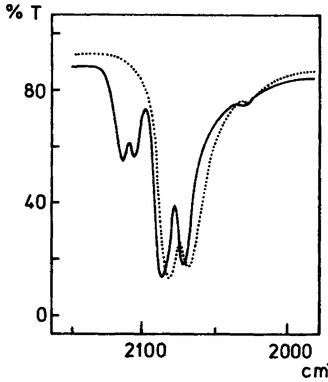

Fig. 3. The infrared spectra of *cis*-[FeL(I)(NCS)$_2$] in the CN stretching region. ...., Recorded at 300 K; —, recorded at 77 K. The optical resolution is ±1 cm^{-1}.

temperature spectrum shows lines both in the high-spin region (2080 and 2071 cm^{-1}), and in the low-spin region (2114 and 2105 cm^{-1}). In the case of *cis*-[Fe L(II)(NCS)$_2$], lines at both regions can be seen even at room temperature (2104(sh), 2098(sh) 2083, 2074 cm^{-1}). Therefore, we conclude that the present transitions are characterized by the coexistence of the high-spin ground state around and below the transition temperature T_c, ruling out any antiferromagnetic binuclear structure or any kind of admixed spin states. Thus *cis*-[FeL(I)(NCS)$_2$] and *cis*-[FeL(II)(NCS)$_2$] are seen to be spin-crossover systems also according to the IR criterium.

The increase in the C−N stretching frequencies of the NCS$^-$ ligand in the spin-crossover system by 30−35 cm^{-1} when going from high-spin to low-spin is comparable to what have been observed for other similar systems,[4] whereas the intermediate spin systems are only shifted by 20−30 cm^{-1} compared to the high-spin systems.

We have suggested that the increase in the ν_{NC} can be explained mainly as due to an increase of the σ-donation when going from high-spin to low-spin.[4]

Comparison of the systems. The variation of the spin transition temperature T_c through the present series of complexes can be rationalized from steric and inductive effects of the methyl-substituents in the amine ligands.

Fig. 1 shows the various modifications of the ligand system dealt with in this work. The parent compound, *cis*-[FeL(I)(NCS)$_2$] is, from the IR spectra, seen to be symmetric, either *cis* or *trans*. With this ligand the *trans* configuration is very unlikely, mainly because of severe strain in the three meridional fused chelates. The *cis-α* isomer where the two pyridine terminals are *trans* to each other is the only configuration having no meridional fused chelates. This is probably also the reason why this isomer is the only one obtained by the reaction of Cr (III) with L(I).[10] It is assumed that all the complexes in this work has the *cis-α* configuration.

The L(I) complex is a spin-crossover system like the bipy and phen complexes, dispite the fact that no conjugated dimine functions are present in the L(I) ligand. This suggests that the additional chelate-ring in coordinated L(I) compared to two coordinated bipy or phen ligands, have compensated for the expected decrease in π-acceptor ability.

The complexes *cis*-[FeL(III)(NCS)$_2$] (R_1 or $R_1'=CH_3$) and *cis*-[FeL(V)(NCS)$_2$] (R_1 and $R_1'=CH_3$), where a methyl group is substituted in the 6 position of the pyridine rings, are pure high-spin complexes within the temperature range used. The high-spin nature of these complexes are probably due to *intra*-molecular nonbonding interactions between the 6-methyl group and isothiocyanate groups, resulting in an increase of the Fe−N distances and a reduction in the ligand field strength. The same argument was used to explain that *cis*-[Fe(2-CH$_3$-phen)$_2$(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(III) and L(V) cases. However, if the CH$_3$ groups are substituted onto the amine nitrogens as in L(IV) ($R_2=CH_3$) no steric interactions are present in the complexes, and the electronic effect is expected *a priori* to dominate. Nevertheless, *cis*-[FeL(IV)(NCS)$_2$] is high-spin in the whole temperature range 4−300 K. This effect might be explained within the framework of the theory that the 2-pyridylmethylamine chelate ring exhibit an electronic hyper-conjugation.[12] Substituting CH$_3$ for H in the chelate ring is expected to break the conjugation, resulting in a decrease in the π-acceptor ability.

Expansion of one chelate ring from five-membered to six-membered, L(I) *vs.* L(II), is expected also to result in a decrease in the ligand field. On the other hand the fusion of two five membered chelate rings is known to give rise to enough strain to distort the ligand field so much that the high-spin state will be favoured.[6] The strain is released if one six-membered ring is fused to one of the five membered rings. The structure given in Fig. 1 (n=3) is expected for *cis*-[FeL(II)(NCS)$_2$]. With a six-membered chelate ring in the complex, however, the meridional structures (*cis-β* and *trans*) cannot be ruled out. On the other hand the IR spectrum suggests a *cis-α* structure for this complex too. It is a spin equilibrium system with T_c at a temperature at 100 K higher than for the corresponding L(I) complex. So, just as has been seen for the iron(II) complexes of the hexadentate ligands tpen and tptn,[6] the ligand field strengths are highest for the strain-free systems.

EXPERIMENTAL

Instruments. Magnetic susceptibilities were measured by the Faraday method, using Hg [Co (SCN)$_4$] as calibrant. The equipment has been described elsewhere.[15] The molar susceptibilities were corrected for ligand diamagnetism by Pascal's constant.[16] 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 vacuum on a cold finger cooled with liquid nitrogen.

Preparations of ligands. N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine* (L(IV)). This ligand was prepared by a method which was a slight modification of Anderegg's method.[5] A solution of 2-pyridylmethyl chloride hydrochloride prepared from α-picoline[17] (16.4 g 100 mmol) in water (10 ml) was neutralised with a sodium hydroxide solution (20 ml, 5 M) and *N,N'*-dimethyl-1,2-ethanediamine (Aldrich) 4.4 g, 50 mmol) was added. During the following days a sodium hydroxide solution (20 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) highvacuum distillation. The product was a yellow viscous oil, 4.2 g (31 %).

N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine* [L(II)]. N*-(6-Methyl-2-pyridylmethyl)-*N'*-(2-pyridylmethyl)-1,2-ethanediamine* [L(III)]. N,N'*-bis(6-Methyl-2-pyridylmethyl)-1,2-ethanediamine.* [L(V)]. These ligands were all obtained as intermediates in the preparation of hexadentate ligands of the tetrakis(2-pyridylmethyl)- 1,2-ethanediamine type by Toftlund and Yde-Andersen.[6]

N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine* [L(I)] was obtained analogously from 1,2-ethanediamine and 2-pyridinecarbaldehyde (Aldrich).

All the ligands were purified by high vacuum distillation. The products were yellow viscous oils, yields 30–40 %.

Peparation of Iron(II) Complexes. A solution of iron(II) sulfate (1.4 g, 5 mmol) in water (20 ml) and a solution of the ligand (5 mmol) in ethanol (20 ml) were both heated to 50 °C and flushed with N$_2$. The ligand solution was added with stirring to the iron(II) solution and immediately after a solution of potassium thiocyanate (1 g, 10 mmol) in a few ml water was added. The solution was slowly cooled to room temperature. The precipitated iron(II) complex was filtered off and washed with water and once with cold ethanol. Drying in a vacuum yielded in all cases about 1.5 g (about 75 %). (Anal. C,H,N,S).

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REFERENCES

1. Gütlich, P. *Struct. Bonding (Berlin) 44* (1981) 83.
2. Cunningham, A. J., Fergusson, J. E. and Powell, H. K. J. *J. Chem. Soc. Dalton Trans.* (1972) 2155.
3. Madeja, K., Böhmer, W. M., Nguyen-Tong Thúy, Oehme, G., El-Saghier, A., Vertes, A. and Burger, K. *Z. Anorg. Allg. Chem. 447* (1978) 5.
4. Højland, F., Toftlund, H. and Yde-Andersen, S. *Acta Chem. Scand. A 37* (1983) 251.
5. Anderegg, G. and Wenk, F. *Helv. Chim. Acta 50* (1967) 2330.
6. Toftlund, H. and Yde-Andersen, S. *Acta Chem. Scand. A 35* (1981) 575.
7. Müller, E. W., Spiering, H. and Gütlich, P. *Chem. Phys. Lett. 93* (1982) 567.
8. Baker, W. A., Jr. and Long, G. J. *Chem. Commun. 15* (1965) 368.
9. König, E. and Madeja, K. *Inorg. Chem. 6* (1967) 48.
10. Michelsen, K. *Acta Chem. Scand. A 31* (1977) 429.
11. Fleisch, J., Gütlich, P., Hasselbach, K. M. and Müller, W. *Inorg. Chem. 15* (1976) 958.
12. Hancock, R. D. and McDougall, G. J. *J. Chem. Soc. Dalton Trans.* (1977) 67.
13. König, E. *J. Inorg. Nucl. Chem. 34* (1972) 2877.
14. Dockum, B. W. and Rieff, W. M. *Inorg. Chim. Acta 35* (1979) 285.
15. Pedersen, E. *Acta Chem. Scand. 26* (1972) 333.
16. Mulay, L. N. and Boudreaux, E. A. *Theory and Applications of Molecular Diamagnetism,* Wiley, London 1976.
17. Mathes, W. and Schültly, H. *Angew. Chem. 75* (1963) 235.

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