

Spin Equilibria in Octahedral Iron(II) Complexes with Some Hexadentate Ligands of the Tetrakis(2-pyridylmethyl)ethylenediamine Type and a Spectral Correlation With Their Cobalt(III) and Nickel(II) Analogs

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The preparations of the new amines N,N,N',N' -tetrakis(2-pyridylmethyl)propylenediamine (= tppn), N,N,N',N' -tetrakis(2-pyridylmethyl)trimethylenediamine (= tptn), N,N,N',N' -tetrakis(2-pyridylmethyl)-*trans*-1,2-cyclohexanediamine (= tpchxn), N -(6-methyl-2-pyridylmethyl)- N,N',N' -tris(2-pyridylmethyl)ethylenediamine (= ltpen) and N,N' -bis(6-methyl-2-pyridylmethyl)- N,N' -bis(2-pyridylmethyl)ethylenediamine (= blbpen) and their complexes with iron(II), cobalt(III) and nickel(II) are described.

Magnetic susceptibility measurements over the temperature range 300–400 K of $[\text{FeL}](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ are reported, L are the ligands mentioned above and N,N,N',N' -tetrakis(2-pyridylmethyl)ethylenediamine (= tpen). The results show that the complexes of iron(II) with $L = \text{tpen}$, tppn, and tpchxn exist in a temperature-dependent high-spin $^5T_2 \rightleftharpoons$ low-spin 1A_1 equilibrium with spin transition-temperatures $T_C = 380$ K for $[\text{Fe}(\text{tpen})]^{2+}$, 492 K for $[\text{Fe}(\text{tppn})]^{2+}$ and 445 K for $[\text{Fe}(\text{tpchxn})]^{2+}$. The complexes of iron(II) with $L = \text{tptn}$ are low-spin and $L = \text{blbpen}$ are high-spin over the temperature range investigated.

The electronic spectra of the iron(II) complexes show that the critical value of $\Delta_{h.s.}$ where 1A_1 becomes the ground state, is 12.6 kK in accordance with predictions based on the electronic spectra of the nickel(II) complexes. ^{13}C NMR spectra of the cobalt(III), Ru(II) and Zn(II) complexes demonstrate that the ligands are hexadentate and that the complexes have pseudooctahedral symmetry.

The temperature-dependent low-spin (1A_1) \rightleftharpoons high-spin (5T_2) transitions in iron(II) complex compounds have been a subject of extensive interest within the

last few years.¹ Apart from a few examples all the investigated systems are with diimine ligands.

In order to get a better understanding of some of the requirements a ligand must fulfil to give a spin-crossover system with iron(II), we decided to make a systematic investigation on multidentate ligands containing aliphatic amines and substituted pyridines as ligating groups. Multidentate ligands are especially desirable in order to enhance the stability of the complexes in solution and to ensure that the magnetic properties of the iron(II) complexes in the solid state reflect the molecular spin-equilibrium phenomena more than collective spin-phase-transitions in the lattice.

Along these lines we have synthesized a series of homologous hexadentate ligands analogous to the N,N,N',N' -tetrakis(2-pyridylmethyl)ethylenediamine (tpen), first investigated by Anderegg.² Some anomalous properties of the $[\text{Fe}(\text{tpen})]^{2+}$ ion could suggest that this ion exhibits spin-crossover behavior.³

In the present work this is confirmed for the perchlorate salt $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. Furthermore the new analogous salts: $[\text{Fe}(\text{tppn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (tppn = N,N,N',N' -tetrakis(2-pyridylmethyl)-1,2-propylenediamine), and $[\text{Fe}(\text{tpchxn})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (tpchxn = N,N,N',N' -tetrakis(2-pyridylmethyl)-1,2-*trans*-cyclohexanediamine are shown to exhibit spin equilibrium behavior, whereas $[\text{Fe}(\text{tptn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (tptn = N,N,N',N' -tetrakis(2-pyridylmethyl)trimethylenediamine) is low-spin and $[\text{Fe}(\text{blbpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (blbpen = N,N' -bis(6-methyl-2-pyridylmethyl)- N,N' -bis(2-pyridylmethyl)ethylenediamine) is high-spin.

Molecular and electronic structures of the iron(II) complex ions in solution are correlated to their nickel(II) and cobalt(III) analogs.

As predicted by Orgel²⁰ there is a forbidden range between the lowest possible Δ for low-spin $\Delta_{l.s.}$ and the highest possible Δ for high-spin $\Delta_{h.s.}$.

RESULTS AND DISCUSSIONS

Preparations. The three new hexadentate ligands, tetrakis(2-pyridylmethyl)propylenediamine (tppn), tetrakis(2-pyridylmethyl)trimethylenediamine (tptn) and tetrakis(2-pyridylmethyl)-*trans*-1,2-cyclohexanediamine (tpchxn), analogous to tetrakis(2-pyridylmethyl)ethylenediamine (tpen) were prepared by reaction of the diamines with an excess of (2-pyridylmethyl)chloride in ethanol, which are modifications of the method used by Anderegg.² We found it more convenient to purify the free bases by recrystallization from petroleum ether than by working up the perchlorates.

The ligands 6-methyl-2-pyridylmethyl-tris(2-pyridylmethyl)ethylenediamine (ltpen) and bis(6-methyl-2-pyridylmethyl)-bis(2-pyridylmethyl)ethylenediamine (blbpen) were prepared in two steps involving reductions of Schiff-bases of the diamine and substituted 2-pyridinecarbaldehydes with sodium tetrahydridoborate. The remaining 2-pyridylmethyl groups were introduced using (2-pyridylmethyl)chloride, as for the other ligands. The perchlorates of the iron(II) complexes were easily obtained in high yields from aqueous iron(II) perchlorate solutions by addition of the equimolar amounts of the free bases. The colours of the salts vary from bright yellow for $[\text{Fe}(\text{blbpen})](\text{ClO}_4)_2$ to dark red for $[\text{Fe}(\text{tptn})](\text{ClO}_4)_2$.

All these iron(II) complexes are stable and resist air oxidation for years in the solid state at room temperature. This is in marked contrast to, for instance, the tris(2-pyridylmethyl)amine iron(II) chloride which is destroyed within a few days when exposed to atmospheric air at room temperature.

The perchlorates of the nickel(II) complexes were obtained analogously.

The ruthenium(II) complexes were obtained by refluxing a mixture of the free bases and ruthenium(III) chloride dissolved in 1,2-propanediol.

The cobalt(III) complexes were obtained in good yields by letting *trans*-[Copy₄Cl₂]Cl, dissolved in methanol, react with the free bases. This procedure gave luteo complexes, which could be precipitated

as perchlorates except for the case where the ligand was blbpen. In that case the main product was a blue cobalt(III) complex with one coordinated chloride, which was isolated as a hexafluorophosphate. This complex was slowly converted to the red hexadentate species in warm neutral aqueous solution.

All the ligands and their metal complexes have been completely characterized by elemental analysis, U.V.-Visible, C.D. spectroscopy and by ¹³C NMR measurements for the nonparamagnetic species.

Analytical data show good agreement between found and calculated values for all the ligands and their metal complexes. In all cases the metal/ligand ratios are 1.

¹³C NMR spectra. The ¹³C NMR spectra for the $[\text{Fe Ligand}]^{2+}$ series (Ligand = tpen, tppn, tpchxn, ltpen and blbpen) are dominated by large line broadenings due to the paramagnetic properties of these species in solution. On the other hand, the spectrum of the low spin complex $[\text{Fe}(\text{tptn})]^{2+}$ shows narrow lines and the whole spectrum looks like that of the corresponding Co(III) complex, suggesting a common structure of the complexes. We assume that the behavior of the $[\text{Co Ligand}]^{3+}$ series reflects the properties of the low-spin $[\text{Fe Ligand}]^{2+}$ series.

The ¹³C NMR spectra of the cobalt(III) complexes offer a most convincing demonstration of a hexadentate monomeric structure for all the low-spin systems in solution (Fig. 1).

The proton decoupled ¹³C NMR spectra for the $[\text{Co}(\text{tpen})]^{3+}$ and $[\text{Co}(\text{R-tppn})]^{3+}$ complexes are shown in Fig. 2.

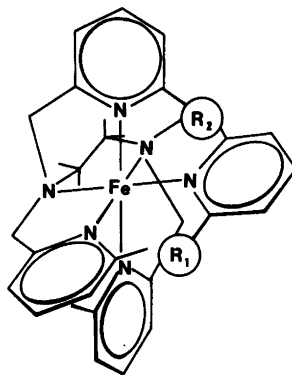


Fig. 1. Drawing of the tetrakis(2-pyridylmethyl)ethylenediamine iron(II) $[\text{Fe}(\text{tpen})]^{2+}$ framework. R_1 and R_2 are the two possible positions for CH_3 in the ltpen complexes.

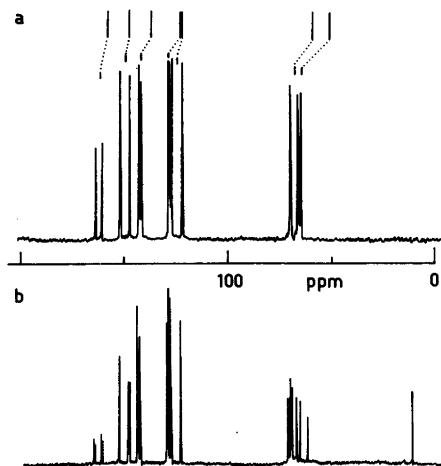


Fig. 2. The proton decoupled 15.03 MHz ^{13}C NMR spectra of *a* $[(\text{Co}(\text{tpen}))(\text{ClO}_4)_3]$ and *b* $[\text{Co}(\text{tppn})](\text{ClO}_4)_3$. The inserted sticks in *a* represent the positions of the corresponding lines for the ligand.

In the complexes containing a symmetrical ligand (tpen, tpchxn, tptn and blbpen), an equivalence of C atoms is retained, corresponding to the presence of a C_2 axis in the complex ions, ruling out the possibility of five-coordination in these cases.

It is seen that the picolyl signals are split as expected for a fixed pseudo-octahedral structure (Fig. 1) for which the picolyl-groups in the diamine plane (*equatorial*) are non-equivalent with the picolyl-groups, above and below this plane (*axial*).

The presence of two types of picolyl-C signals excludes the possibility of a fluxional behavior within the NMR time scale, for these complexes. As the conformation of the aliphatic diamine chelate ring is locked when the pyridine ends of the ligand are ligating, no ring inversion ($\delta \rightleftharpoons \lambda$) is possible. This is also exhibited in the spectrum of the $[\text{Co}(\text{R-tppn})]^{3+}$ which shows only one methyl-C signal, arising, no doubt, from the methyl group in an *equatorial* position, because of the severe crowding which would have occurred in an isomer with the methyl in *axial* position. The same stereospecificity has been observed for the cobalt(III) complexes of tetrakis(2-aminoethyl)-*R*-propylenediamine $[\text{Co}(\text{R-Me-penten})]^{3+}$.⁴

The further splitting of several of the lines in the ^{13}C NMR spectrum of $[\text{Co}(\text{R-tppn})]^{3+}$, compared to the spectrum of $[\text{Co}(\text{tpen})]^{3+}$ (Fig. 2), is a con-

sequence of the asymmetric nature of the aliphatic diamine resulting in a destruction of the C_2 axis of the complex ion.

It is interesting that the ^{13}C NMR spectra of both $[\text{Co}(\text{tpen})]^{3+}$ and $[\text{Co}(\text{blbpen})]^{3+}$ exhibit only one methyl signal from the lutedyll groups, showing that only one isomer is formed for each complex. We assume that the lutedyll end takes the *equatorial* positions, as this will give the least crowded coordination, as judged from molecular models. As expected, the blue $[\text{Co}(\text{blbpen})\text{Cl}]^{2+}$ complex shows a very complicated spectrum with no equivalent C atoms confirming that in this case the ligand is five coordinated.

For all the Co(III) complexes the ^{13}C NMR lines are shifted downfield, compared to the respective free ligands. In Table 1 these shifts are presented for carbon atom 4 in the heterocyclic rings within the Co(III) complexes and some Zn(II) and Ru(II) complexes. It has been suggested that these shifts reflect the electron donor properties of substituted pyridine ligands.⁵ σ -Donation leads to downfield shifts ($\Delta\sigma$ pos) whereas π -back-donation leads to an upfield shift. From Table 1 it is apparent that all the Co(III) complexes, except $[\text{Co}(\text{blbpen})]^{3+}$, has $\Delta\delta$ in the narrow range $+5.3 < \Delta\delta < 6.2$ suggesting comparable electron-donor properties, in this case mainly σ -donation. blbpen, which shows a much smaller shift when coordinated to Co(III), is from this criterion expected to be a poor σ -donor in spite of the inductive effect from the methyl groups. As will be demonstrated below blbpen gives rise to a smaller ligand field than do the other ligands in the series.

Spin pairings are known to be promoted by ligands which are good π -back-donors. In order to get an estimate of the relative π -back-donor properties of the ligands dealt with in this work we made the ruthenium(II) complex, $[\text{Ru}(\text{tpen})]^{2+}$, and recorded its ^{13}C NMR spectrum. From Table 1 it is seen that the signals from C_4 are shifted upfields, as expected for systems stabilized by a strong π -back-donation. That π -back-donation indeed is important in $[\text{Fe}(\text{tptn})]^{2+}$, is seen from the small $\Delta\delta = 0.68$ ppm which is much less than the value of 3.94 ppm, observed for $[\text{Zn}(\text{tptn})]^{2+}$.

Magnetic measurements. The susceptibility measurements were made on solid samples in the temperature range 300–400 K, except in the case of $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ which were measured down to 100 K.

All measurements were made at three different

Table 1. ^{13}C NMR data for the 4-carbon atom in the ligands and some complexes in methanol.

Compound	Chemical shifts in ppm	$\Delta\delta\text{m}^a$
tptn	138.07	
$[\text{Co}(\text{tptn})](\text{ClO}_4)_2$	144.21, 143.38	5.73
$[\text{Fe}(\text{tptn})](\text{ClO}_4)_2$	138.75	0.68
$[\text{Zn}(\text{tptn})](\text{ClO}_4)_2$	142.01	3.94
tppn	138.10	
$[\text{Co}(\text{tppn})](\text{ClO}_4)_3$	144.54, 143.31	5.83
tpchxn	137.58	
$[\text{Co}(\text{tpchxn})](\text{ClO}_4)_3$	144.34, 143.05	6.12
tpen	137.75	
$[\text{Co}(\text{tpen})](\text{ClO}_4)_3$	143.59, 142.49	5.29
$[\text{Ru}(\text{tpen})](\text{ClO}_4)_2$	137.68, 136.44	-0.69
ltpen	138.16	
$[\text{Co}(\text{ltpen})](\text{ClO}_4)_3$	144.34, 143.76, 143.25	5.62
blbpen	138.13	
$[\text{Co}(\text{blbpen})](\text{ClO}_4)_3$	142.14, 141.69	3.79
$[\text{Co}(\text{blbpen})\text{Cl}](\text{ClO}_4)_2$	141.30, 141.14, 140.79, 137.19	1.98

^a Chemical shift for the average C_4 in the complex minus C_4 for the ligand.

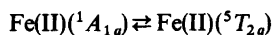
field strengths and in no case was any field dependence observed. Moreover, the data were recorded with both descending and ascending temperatures and there was no evidence of thermal hysteresis. The compounds showed signs of decomposition at temperatures above 400 K.

The temperature dependence of the effective magnetic moment, μ_{eff} , of the six iron(II) compounds displays a variation from that of a typical high-spin complex to that of a typical low-spin complex. The molar susceptibility of $[\text{Fe}(\text{tptn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was constant 225×10^{-6} (± 25) cg s mol^{-1} in the temperature interval studied. This gives a room temperature magnetic moment of 0.75 BM, a normal value of a low-spin pseudooctahedral iron(II) complex.¹² However, strongly temperature dependent magnetic moments were observed for $[\text{Fe}(\text{tppn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\text{Fe}(\text{tpchxn})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. The last compound has been measured earlier³ in the temperature interval 76–298 K. We have repeated these measurements and extended the temperature interval to 400 K. Over the range from 100 K to 400 K the effective magnetic moment of $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ varied from 0.38 BM to 4.10 BM. We interpret this behavior as a "spin equilibrium" with an $^1A_{1g}(t_{2g}^6)$ and a $^5T_{2g}(t_{2g}^4e_g^2)$ state both thermally accessible in the temperature range studied. This conclusion

is supported by the results from the NMR spectra (see above) and the electronic spectra (see below). The complexes $[\text{Fe}(\text{tppn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Fe}(\text{tpchxn})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ were observed to exhibit similar behavior and can therefore also be classified as spin equilibrium systems. The effective magnetic moment of $[\text{Fe}(\text{ltpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ varied from 4.70 BM at 100 K to 5.08 BM at 400 K. The relatively small temperature variation of the magnetic moment suggests the existence of two types of high-spin molecules of which only one exhibits spin transition behavior. From the present data we cannot decide if the effect is due to the presence of both geometrical isomers or that the lattice has two non-equivalent sites for the same cation. The latter possibility has been suggested in order to explain similar data for $[\text{Fe}(\text{2-CH}_3\text{phen})_3](\text{ClO}_4)_2$.⁶ The last compound $[\text{Fe}(\text{blbpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ exhibits a behavior, typical for a high-spin pseudooctahedral iron(II) complex with a constant magnetic moment of 5.25 BM in the temperature range studied.

Theoretical expressions for the temperature dependence of the magnetic susceptibility of spin equilibrium complexes has been reported in detail.¹⁹ In all of these cases a Boltzmann distribution over the lowest available states has been assumed. In general, models based on this assumption have

proven inadequate without the addition of extra parameters. This is also the case for the complexes described here. The other approach,⁷ which has been employed to interpret the temperature dependence of the magnetic susceptibility is an empirical one. Thermodynamic parameters for the equilibrium



are evaluated using the equation

$$K_{\text{eq}} = \frac{\chi_m - \chi_{\text{hs}}}{\chi_{\text{hs}} - \chi_m} \quad (1)$$

where χ_m is the experimental molar susceptibility at a given temperature, while χ_{hs} and χ_{ls} are the molar susceptibilities of the pure high-spin and

pure low-spin components at the same temperature. The results obtained for $[\text{Fe}(\text{blbpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Fe}(\text{tptn})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ were used as χ_{hs} and χ_{ls} . Only the linear parts of the $\ln K$ vs. $1/T$ plots have been used in the calculations of the thermodynamic parameters. The results are given in Table 2.

The variation of the spin transition-temperature T_C through the present series of complexes, can be rationalized from the steric and inductive effects of the substituents in the tetrakis(2-pyridylmethyl)-diamine framework. The well-established fact that (2-pyridylmethyl)amine gives tris-complexes with iron(II), which are spin cross-over systems^{8,9,10} might suggest that $[\text{Fe}(\text{tpen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ should be low-spin because of the extra chelate-effect from the fused rings. The behavior shown here is probably a consequence of a distortion of the N_6 -chromophore due to strain in the resulting fused

Table 2. Temperature dependence of the effective magnetic moments μ_{eff} and spin equilibrium constants K_{eq} .

Compound	<i>T</i>	μ_{eff}^a	$\ln K_{\text{eq}}^b$	Compound	<i>T</i>	μ_{eff}^a	$\ln K_{\text{eq}}^b$		
[Fe(tppn)] (ClO ₄) ₂ · H ₂ O ^c	305.1	0.97	-4.21	[Fe(tpchxn)] (ClO ₄) ₂ · 2H ₂ O ^d	305.4	1.15	-3.52		
	314.7	1.04	-3.93		317.2	1.25	-3.26		
	324.3	1.16	-3.53		327.3	1.36	-3.02		
	334.6	1.24	-3.32		337.1	1.57	-2.60		
	345.1	1.37	-3.00		348.9	1.74	-2.32		
	354.0	1.48	-2.80		360.7	2.01	-1.93		
	363.7	1.65	-2.49		369.8	2.24	-1.64		
	375.0	1.89	-2.11		381.1	2.48	-1.36		
	383.5	2.01	-1.94		390.1	2.76	-1.06		
	394.9	2.23	-1.67		402.0	3.05	-0.75		
	403.1	2.37	-1.50						
		99.6	0.38						
	[Fe(tpen)] (ClO ₄) ₂ · H ₂ O ^c	150.5	0.43			[Fe(ltpen)] (ClO ₄) ₂ · H ₂ O ^c	100.7	4.70	
200.4		0.47		150.5	4.76				
256.9		0.77		201.9	4.78				
290.2		1.46		250.9	4.81				
304.9		1.96	-1.97	304.7	4.83				
315.1		2.20	-1.67	317.4	4.88				
327.2		2.60	-1.21	327.0	4.89				
332.0		2.70	-1.11	337.0	4.92				
340.0		2.88	-0.921	349.1	4.95				
348.9		3.14	-0.652	359.2	4.99				
357.3		3.30	-0.486	370.7	5.00				
369.9		3.47	-0.311	382.5	5.04				
381.6		3.80	0.047	393.1	5.06				
392.1		3.95	0.220	403.3	5.08				
412.0		4.22	0.561						

^a $\mu_{\text{eff}} = 2.83 (\chi_m T)^{1/2}$, χ_m is the molar susceptibility corrected for ligand diamagnetism. Experimental uncertainty between ± 0.04 BM and ± 0.08 BM dependent on temperature. ^b Calculated using eqn. 1. ^c $\chi^{\text{dia}} = -360 \times 10^{-6}$ cg s mol⁻¹. ^d $\chi^{\text{dia}} = -404 \times 10^{-6}$ cg s mol⁻¹. ^e $\chi^{\text{dia}} = -350 \times 10^{-6}$ cg s mol⁻¹.

Table 3. Thermodynamic parameters for the spin equilibria.

Compound	ΔH_{eff}^a (kcal · mol ⁻¹)	ΔS_{eff}^a (eu)	T_c (K)
[Fe(tppn)](ClO ₄) ₂ · H ₂ O	6.57	13.4	492
[Fe(tpchxn)](ClO ₄) ₂ · 2H ₂ O	6.81	15.3	445
[Fe(tpen)](ClO ₄) ₂ · H ₂ O	6.11	16.1	380

^a Calculated in the temperature range over which eu K_{eq} vs. $1/T$ plot is linear. ^b T_c ($=\Delta H_{\text{eff}}/\Delta S_{\text{eff}}$) is the temperature of equal fractions of high-spin and low-spin components.⁵

Table 4. Visible-ultraviolet-spectral data for the iron(II) complexes in water at 25 °C.

Compound	Charge transfer		¹ T ₁ ← ¹ A ₁		⁵ E ← ⁵ T ₂		λ_{sh} nm	ϵ_{max}
	λ_{max} nm	ϵ_{max}^a	λ_{max} nm	ϵ_{max}	λ_{max} nm	ϵ_{max}		
[Fe(tptn)](ClO ₄) ₂	425	11310	550	~ 100	—	—	—	—
[Fe(tppn)](ClO ₄) ₂	425	10670	550	~ 100	—	—	—	—
[Fe(tpchxn)](ClO ₄) ₂	419	9706	546	~ 100	—	—	—	—
[Fe(tpen)](ClO ₄) ₂	414	7810	545	~ 100	—	—	—	—
[Fe(ltpen)](ClO ₄) ₂	397	3160	540	~ 60	790	7	1000	4
[Fe(bltpen)](ClO ₄) ₂	359	1640	—	—	839	9	1010	6

^a ϵ in units of 1 mol⁻¹ cm⁻¹.

five five-membered chelate rings.¹¹ The increase of the unique chelate ring from a five to a six-membered ring releases enough strain to stabilize [Fe(tptn)](ClO₄)₂ · H₂O as a low-spin complex. [Fe(tppn)](ClO₄)₂ · H₂O has a lower T_c temperature than that found for [Fe(tpen)](ClO₄)₂ · H₂O. This is caused by the inductive effect of the methyl-substituent in the aliphatic ring. A further increase of the inductive

effect is expected in [Fe(tpchxn)](ClO₄)₂ · 2H₂O but this effect seems to be counteracted by that of the strain arising from fusing the aliphatic cyclohexane ring to the unique chelate-ring. In the two complexes, [Fe(ltpen)](ClO₄)₂ · H₂O and [Fe(bltpen)](ClO₄)₂ · H₂O, where methyl groups are substituted in the 6-position of the pyridine rings, the ⁵T_{2g} state is highly populated. This is not surprising, molecular models (Fig. 1) show that the methyl groups produce *intra*-molecular nonbonding interactions, which increase the Fe–N distances. Similar effects have been observed for the iron(II) complexes of 2-methyl-1,10-penanthroline.⁶

Thus the variation of the magnetic properties through the present series of complexes has been explained by changes in molecular parameters. This conclusion is supported by the interpretation of the electronic spectra of the analogous Co(III) and Ni(II) complexes, as demonstrated below.

Electronic spectra. Attempts to obtain a correlation between ligand field parameters and the magnetic properties of iron(II) complexes, has been complicated by the fact that very intense charge transfer bands in the visible region mask the ligand field transitions in most of the known low-spin systems, the majority of which is of the diimine type. Nelson¹² has shown that bis-(2-pyridymethyl)amine

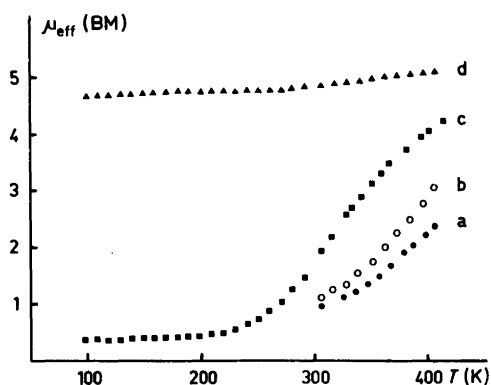


Fig. 3. Temperature dependence of the effective magnetic moments μ_{eff} : a [Fe(tppn)](ClO₄)₂ · H₂O. b [Fe(tpchxn)](ClO₄)₂ · 2H₂O. c [Fe(tpen)](ClO₄)₂ · H₂O. d [Fe(ltpen)](ClO₄)₂ · H₂O.

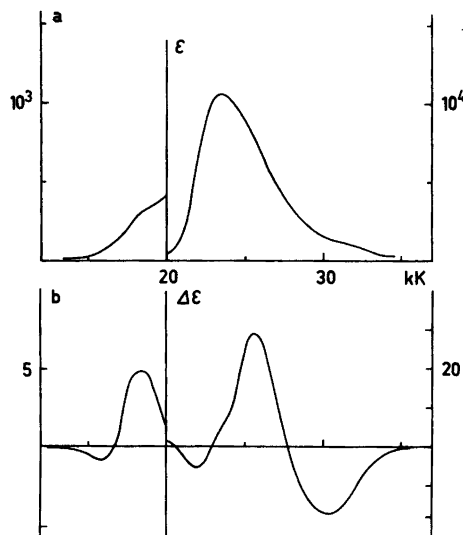


Fig. 4. The visible ultraviolet spectrum of $[\text{Fe}(\text{R-tpnn})](\text{ClO}_4)_2$. *b* The CD spectrum of $[\text{Fe}(\text{R-tpnn})](\text{ClO}_4)_2$ in the same range as *a*.

iron(II), ion $[\text{Fe}(\text{dpa})_2]^{2+}$ is low-spin and exhibits a charge transfer band of high extinction at 23.10 kK, which is considerably blue-shifted compared to the spectra of the diimine iron(II) complexes. The visible absorption spectra of the present $[\text{Fe Ligand}](\text{ClO}_4)_2$ complexes are shown in Table 4 and a typical one, that of $[\text{Fe}(\text{tpnn})](\text{ClO}_4)_2$, is shown in Fig. 4. The spectra profile and extinction coefficients of the charge transfer bands for the tetrakis(2-pyridylmethyl)diamine iron(II) complexes are similar to those of $[\text{Fe}(\text{dpa})_2]^{2+}$ but the maxima are blue-shifted by about 1 kK. The iron(II) complexes of the lutedyl-containing ligands exhibit charge transfer bands with lower extinction coefficient and

they are further blue-shifted. Weak shoulders are seen on the low-energy side of the bands, at a position where the ligand field transitions ${}^1T_{1g} \leftarrow {}^1A_{1g}$ are expected to show up. The assignment is supported by the fact that these bands are absent in $[\text{Fe}(\text{ltpen})]^{2+}$ and $[\text{Fe}(\text{blbpen})]^{2+}$ which from the magnetic measurements are believed to have a ${}^5T_{2g}$ type of ground level. These complexes exhibit weak bands at 12.64 kK and 12.00 kK, respectively, and very weak shoulders at 9.70 kK and 9.40 kK due to ${}^5E_g \leftarrow {}^5T_{2g}$ transitions.

The band at 12.25 kK in $[\text{Fe}(\text{2-pyridylmethylamine})_3]^{2+}$ has been given the same assignment.¹³ The possibility of using an optically active diamine in the preparation of some of the ligands gave the option of obtaining a much more detailed information of the electronic structure of the metal complexes by recording the circular dichroism (CD) spectra. This is shown for $[\text{Fe}(\text{R-tpnn})]^{2+}$ in Fig. 4. The fact that the most intense band at 28.96 kK apparently is forbidden in CD makes it easy to find the position of the two components in the ${}^1T_{1g}$ band. The energies are given in Table 5. From these values the ligand fields strengths $\Delta_{1.s.}$ are calculated to 17.3 for both complexes. The splittings are in both systems estimated to 0.6 kK supporting the assumed pseudo-octahedral symmetry. The found $\Delta_{1.s.}$ values are smaller than the values obtained by Jesson¹⁴ for the iron(II) polypyrazolatoborate complexes known to be in a spin equilibrium between ${}^5T_{2g}$ and ${}^1A_{1g}$ ground states in solution at room temperature.

In these complexes the conformation of the diamine chelate ring determines the absolute configurations of the complexes. As the *R,R*-chxn chelate ring is fixed in a λ conformation and the *R-pn* chelate ring is expected also to adopt a λ conformation. It is expected that the CD spectra of the

Table 5. Circular dichroism spectral data in water at 25 °C.

Compounds	Charge transfer bands	<i>d-d</i> bands
	ν_{ext} kK ($\Delta\epsilon_{\text{ext}}$)	
$[\text{Fe}(\text{R-tpnn})](\text{ClO}_4)_2$	30.40 (−17.10), 25.58 (+28.96), 23.75 (+6.62)	21.98 (−5.52), 18.38 (+4.85), 15.95 (−0.88)
$[\text{Fe}(\text{R,R-tpchxn})](\text{ClO}_4)_2$	30.12 (−8.00), 25.44 (+14.62), 23.42 (+3.45)	21.65 (−2.44), 18.35 (+2.50), 15.95 (−0.73)
$[\text{Co}(\text{R-tpnn})](\text{ClO}_4)_3$	33.22 (−5.64), 28.49 (+0.94)	26.25 (−0.32), 22.27 (−4.85), 20.00 (−1.50)
$[\text{Co}(\text{R,R-tpchxn})](\text{ClO}_4)_3$	32.68 (−2.48), 28.25 (+0.35)	26.04 (−0.25), 22.47 (−1.30), 19.46 (−0.78)

Table 6. Visible—ultraviolet-spectral data for the cobalt(III) complexes in water at 25 °C.

Compound	${}^1T_{2g} \leftarrow {}^1A_{1g}$		${}^1T_{1g} \leftarrow {}^1A_{1g}$		Δ kK	B kK ^b
	λ_{\max} nm	ϵ_{\max} ^a	λ_{\max} nm	ϵ_{\max} ^a		
[Co(tptn)](ClO ₄) ₃	328	sh	465	111	22.58	0.66
[Co(tppn)](ClO ₄) ₃	330	400	470	314	22.33	0.59
[Co(tpchxn)](ClO ₄) ₃	331	400	474	300	22.14	0.61
[Co(tpen)](ClO ₄) ₃	328	400	468	313	22.43	0.61
[Co(ltpen)](ClO ₄) ₃	341	400	483	303	21.73	0.58
[Co(blbpn)](ClO ₄) ₃	355	400	513	252	20.50	0.64

^a ϵ in units of $1 \text{ mol}^{-1} \text{ cm}^{-1}$. ^b Calculated with the assumption that $C/B=4$.

two systems are similar as is indeed seen.

Using the rules recommended by IUPAC¹⁶ to define an absolute configuration, both $[M(R\text{-tppn})]^{n+}$ and $[M(R,R\text{-tpchxn})]^{n+}$ are assigned the absolute configuration "skew chelate pairs" $\Delta\Delta\Delta$. This assignment is in agreement with Gillards assignment of Δ for $(-)[\text{Co}(R\text{-Me penten})]^{3+}$ ⁴ for which the main deflection in the first ligand field band is negative as for $[\text{Co}(R\text{-tppn})]^{3+}$.

By changing the metal ion from iron(II) to the isoelectronic cobalt(III), in the complexes $[M(\text{Ligand})]^{n+}$, the charge transfer bands are blue-shifted so much that the ligand field bands ${}^1T_{2g} \leftarrow {}^1A_{1g}$ are clearly seen. This fact makes it possible to make a correlation between Δ for Co(III) and Fe(II) with the prospect of predicting the critical Δ value for other systems. The spectral data for the Co(III) complexes are given in Table 6. The calculated Δ values are 1.28 times the $\Delta_{1.s.}$ for the corresponding iron(II) complexes ($R\text{-tppn}$, $R,R\text{-tpchxn}$). Based on the Co(III) complexes the critical range, leading to spin-cross behaviour, then is $17.0 < \Delta_{1.s.}(\text{Fe}^{II}) < 17.6$.

The band contours are typical for octahedral complexes. As a matter of fact, the tetrakis(2-pyridylmethyl)diamine cobalt(III) salts look like usual luteo complexes although the second ligand field bands only are seen as shoulders on the charge transfer bands. An analysis of the CD spectra reveals a splitting of 0.5 and 0.7 kK between the two components of the first ligand field bands for $[\text{Co}(R,R\text{-tpchxn})]^{3+}$ and $[\text{Co}(R\text{-tppn})]^{3+}$, respectively, corresponding to small distortions of the chromophores. Even the red $[\text{Co}(l\text{tpen})]^{3+}$ and $[\text{Co}(blbpn)]^{3+}$ appear to have relatively high symmetries. However, the intensities of the first ligand field bands for all the complexes, except $[\text{Co}(tptn)]^{3+}$, are three times the value normally seen for luteo complexes. This fact could be a

consequence of a distortion of the chromophores for the cases where the aliphatic diamine chelate rings are five-membered.

Several authors have used a correlation between the magnitude of Δ in nickel(II) complexes to estimate Δ for the corresponding iron(II) complexes, in the cases where their ligand field bands are masked by the charge transfer bands.^{17,12} One drawback in using this method for the determination of the critical $\Delta_{h.s.}$, is that the interesting range of Δ values will be that close to the energetic crossover point of the ${}^3T_{2g}$ and 1E_g energy levels.¹³ As these energy levels cannot coincide the true position of ${}^3T_{2g}$ is difficult to find.¹⁸

Table 7 shows the spectral data for nickel(II) complexes corresponding to the iron(II) complexes described in the present work. The assignments are based on the relative intensities and the expectation that the position of 1E_g should be rather constant. We find the Δ values for the whole series in the range $10.5 < \Delta(\text{Ni}^{II}) < 12.3$ kK. Using a $\Delta_{h.s.}(\text{Fe}^{II})/\Delta(\text{Ni}^{II})$ ratio of 1.05,¹⁷ this range corresponds to $11.0 < \Delta_{h.s.}(\text{Fe}^{II}) < 12.9$ kK in agreement with the direct observation of $\Delta_{h.s.}$ for $[\text{Fe}(l\text{tpen})]^{2+}$ and $[\text{Fe}(blbpn)]^{2+}$ giving $\Delta_{h.s.}=12.64$ and 11.92 kK, respectively. From the magnetic measurements we know that $[\text{Fe}(blbpn)](\text{ClO}_4)_2$ is purely high-spin and $[\text{Fe}(l\text{tpen})](\text{ClO}_4)_2$ 85 % high-spin at room temperature. So the critical range of existence of spin cross systems is quite narrow. We suggest the range $12.3 < \Delta_{h.s.}(\text{Fe}^{II}) < 12.8$ kK for these type of ligands. We are now in the position of giving an estimate of the mean spin-pairing energy for iron(II)

$$\bar{p} = \frac{2.4\Delta_{1.s.} - 0.4\Delta_{h.s.}}{2} = 17.9 \pm 0.6 \text{ kK.}$$

This value is greater than those estimated by Wilson¹⁵ and others¹⁹ but seems to be quite reasonable since $|\Delta_{1.s.} - \bar{p}| \sim 0.6$ kK is a sufficient

Table 7. Visible spectral data for the nickel(II) complexes in a 1:1 water – acetone mixture at 25 °C.

Compound	λ_{\max} nm	ϵ_{\max}^a	λ_{\max} nm	ϵ_{\max}^b	${}^3T_{2g} \leftarrow {}^3A_{2g}$		${}^1E_g \leftarrow {}^3A_{2g}$		${}^3T_{2g} \leftarrow {}^3A_{2g}$	
					ν_{kk}	ν_{kk}	ν_{kk}	ν_{kk}	Δ kK	B kK
[Ni(tptn)](ClO ₄) ₂	805	11.0	510	10.5	11.99	12.50	19.61	12.25	0.64	
[Ni(tppn)](ClO ₄) ₂	822	26.4	517	16.9	11.29	12.29	19.34	11.36	0.67	
[Ni(tpchxn)](ClO ₄) ₂	816	29.0	518	18.7	11.26	12.39	19.31	11.33	0.67	
[Ni(tpen)](ClO ₄) ₂	822	22.5	517	13.5	11.20	12.33	19.34	11.27	0.68	
[Ni(ltpen)](ClO ₄) ₂	929	25.1	527	14.0	10.75	12.23	18.98	10.81	0.69	
[Ni(blbpn)](ClO ₄) ₂	963	26.7	551	10.6	10.38	12.06	18.15	10.42	0.65	

^a ϵ in units of $1 \text{ mol}^{-1} \text{ cm}^{-1}$. ^b Estimated after a deconvolution of the band in Gaussian components.

condition for observing the spin equilibrium phenomenon in solution at room temperature. A more detailed study of this equilibrium for some of the systems in this work is now in progress.

In agreement with the predictions by Orgel²⁰ we found a discontinuous change of Δ going from high-spin to low-spin. Thus $\Delta_{\text{l.s.}}$ is 38 % larger than $\Delta_{\text{h.s.}}$ for the cross-over systems in the present work.

EXPERIMENTAL

Instruments. Magnetic susceptibilities were measured by the Faraday method. The equipment employs a 100 mm electromagnet (Bruker-Physik) with Henry-type pole caps, an electrical microbalance (Sartorius type 411), and the required cryogenic equipment. Temperatures were measured using a chromel-alumel thermocouple. The molar susceptibilities were corrected for ligand diamagnetism by Pascal's constants.²¹

A Zeiss DMR 21 spectrophotometer or A Cary 219 spectrophotometer were used for spectrophotometric measurements in the visible and near IR region. Circular dichroism spectra were measured with a Jouan Dichrographe 2B. Proton-decoupled 15.03 MHz ¹³C NMR spectra were measured with a JEOL FX-60 NMR Spectrometer.

Preparation of Ligands

Tetrakis(2-pyridylmethyl)ethylenediamine (tpen). This ligand was prepared by a method which was a modification of Anderegg's method.² To a solution of pure (2-pyridylmethyl)chloride prepared from α -picoline² (19 g, 149 mmol) in water (50 ml) was added ethylenediamine (2.4 ml 36 mmol). During the following 4 days a sodium hydroxide solution (37 ml 4 M) was added with stirring in so small portions that pH never exceeded 9. The remaining mixture was extracted with chloroform. A dark red crude product of the tetrakis(2-pyridylmethyl)-

ethylenediamine was obtained by evaporation of the dried chloroform solution. This product was recrystallized from light petroleum (b.p. 50–70 °C) (200 ml) Yield of pure tpen: 5 g (30 %).

Tetrakis(2-pyridylmethyl)-trans-1(R),2(R)-cyclohexanediamine (R,R-tpchxn). This ligand was prepared analogously from 1(R),2(R)-trans-cyclohexanediamine (2 g, 17.5 mmol) Yield; 4,2 g (31.2 %).

R-(+)-Tetrakis(2-pyridylmethyl)-1,2-propanediamine (R tppn) and tetrakis(2-pyridylmethyl)-1,3-propanediamine (tptn). Pure R-(-)-1,2-propanediamine (3.7 g, 50 mmol) prepared as described in the literature,²² or 1,3-propanediamine (R. de Haen) (3.7 g, 50 mmol) was allowed to react with 2-pyridinecarbaldehyde (Aldrich) (10.5 g, 98 mmol) in absolute ethanol (30 ml) by refluxing the mixture for 10 min. The mixture was evaporated under reduced pressure and the residue was dissolved in absolute ethanol (50 ml). To this solution sodium tetrahydridoborate (5 g, 0.132 mol) was added in small portions over a period of 3 h. The solution was left overnight and warmed to boiling point for 1 h. To the resulting solution hydrochloric acid (15 ml 12 M) was added and when the gas evolution had ceased, the solution was made alkaline with a sodium hydroxide solution (20 ml 5 M). Precipitated sodium borate was filtered off and the volume of the filtrate was reduced by evaporation under reduced pressure. The remaining solution was extracted with chloroform. Crude products of R-(+)-bis(2-pyridylmethyl)-1,2-propanediamine or bis(2-pyridylmethyl)-1,3-propanediamine were obtained by evaporation of the dried chloroform solutions. These products were dissolved in absolute ethanol (20 ml) and pure (2-pyridylmethyl)chloride hydrochloride (16 g, 0.125 mol) was added in small portions with stirring. During the following 4 days a sodium hydroxide solution (20 ml 5 M) was added in so small portions that pH never exceeded 9. The precipitated sodium chloride was filtered off and the solution was evaporated to dryness. The dark red residue was extracted with boiling light petroleum (50–70 °C) (2 times 100 ml) and after

cooling to room temperature, the solution was left overnight. The precipitated products were filtered off. Yield of pure *R*-(–)-tppn; 3 g (13.7 %); yield of pure tptn; 4 g (18.3 %).

(6-Methyl-2-pyridylmethyl)tris(2-pyridylmethyl)ethylenediamine (ltpen). This ligand was prepared analogously to (tptn) from 6-methyl-2-pyridine-carbaldehyde (Aldrich) (6.1 g, 50 mmol), 2-pyridylmethylchloride hydrochloride (19.2 g, 150 mmol) and ethylenediamine (3.3 ml, 50 mmol). Yield of ltpen; 8.2 g (37 %).

Bis(6-methyl-2-pyridylmethyl)bis(2-pyridylmethyl)ethylenediamine (blbpen). This ligand was prepared analogously to (tptn) from ethylenediamine (3.3 ml, 50 mmol), 6-methyl-2-pyridinecarbaldehyde (Aldrich) (12.2 g, 100 mmol) and (2-pyridylmethyl)chloride hydrochloride (12.8 g, 100 mmol). Yield of blbpen; 9.1 g (40 %).

Nickel(II) complexes. To a 1:1 methanol–water solution (10 ml) of nickel (II) perchlorate (0.366 g, 1 mmol) heated to 50 °C, the ligand (1 mmol) was added with stirring. The violet solution was slowly cooled to room temperature and the precipitated nickel(II) complex perchlorate was filtered off and washed with ice-cold water.

Drying in air yielded in all cases about 0.5 g (about 75 %).

Iron(II) complexes. A 1:1 methanol–water mixture (10 ml) was flushed with nitrogen. To this solution a few drops of perchloric acid (1 M) and iron wool (ca. 0.5 g) was added. Iron(II) perchlorate hexahydrate (Veba Chem) (0.363 g, 1 mmol) was added and after a few min heating to 50 °C the iron wool was removed from the solution. To the hot solution the ligand (1 mmol) was added with stirring and the solution was slowly cooled to room temperature. The precipitated iron(II) complex perchlorate was filtered off and washed with ice-cold water. Drying in air yielded in all cases about 0.5 g (about 75 %). (Anal. C, H, N, Cl).

Cobalt(III) complexes. *trans*-Dichloro-tetrakis(pyridine)cobalt(III) chloride, $[\text{Co py}_4\text{Cl}_2]\text{Cl}$ aq (0.59 g, 1 mmol) was dissolved in methanol (10 ml). To this solution the ligand (1 mmol) was added with stirring. The color changed from green to yellow-brown and the solution was heated to 50 °C for 5 min. The solution was then evaporated under reduced pressure and the residue was dissolved in water (10 ml). To the resulting solution saturated sodium perchlorate (2 ml) was added and after cooling for one h, the mixture was filtered.

The products were recrystallized from a 1:1 methanol–water mixture. Drying in air yielded: $[\text{Co}(\text{tpen})](\text{ClO}_4)_3$ 0.6 g (75 %); $[\text{Co}(\text{tptn})](\text{ClO}_4)_3$ 0.5 g (61 %); $[\text{Co}(\text{R-tppn})](\text{ClO}_4)_3$ 0.5 g (61 %); $[\text{Co}(\text{R,R-tpchxn})](\text{ClO}_4)_3$ 0.6 g (69 %); $[\text{Co}(\text{ltpen})](\text{ClO}_4)_3$ 0.5 g (61 %).

$[\text{Co}(\text{blbpen})\text{Cl}](\text{PF}_6)_2$. *trans*- $[\text{Co py}_4\text{Cl}_2]\text{Cl}$ aq

(3 g, 5.1 mmol) was dissolved in methanol (30 ml) and to this solution blbpen (2.3 g, 5.0 mmol) was added. The solution was heated to 50 °C for 5 min. By addition of sodium hexafluorophosphate (5 g), a blue salt precipitated. This salt was filtered off and washed with methanol. Drying in air yielded 3.5 g (94 %) (Anal. C, H, N, Cl).

$[\text{Co}(\text{blbpen})](\text{PF}_6)_3$. $[\text{Co}(\text{blbpen})\text{Cl}](\text{PF}_6)_2$ (2 g, 2.7 mmol) was dissolved in a boiling ethanol–water mixture 1:10 (50 ml) and the solution was refluxed for 30 min. After cooling to room temperature a little unchanged $[\text{Co}(\text{blbpen})\text{Cl}](\text{PF}_6)_2$ was filtered off. The volume of the filtrate was reduced to 10 ml and sodium hexafluorophosphate (1 g) was added. The red salt was filtered off and washed with a little cold methanol. Drying in air yielded, 1.6 g (62 %).

Acknowledgement. The authors are grateful to Dr. Erik Pedersen for the low temperature magnetic susceptibility measurements on $[\text{Fe}(\text{ltpen})](\text{ClO}_4)_2$ and the CD spectra. Furthermore he is thanked for helpful discussions.

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Received January 30, 1981.