Quadridentate *versus* Quinquedentate Co-ordination of some N_5 and N_3O_2 Macrocyclic Ligands and an Unusual Thermally controlled Quintet $\rightleftharpoons$ Singlet Spin Transition in an Iron(II) Complex

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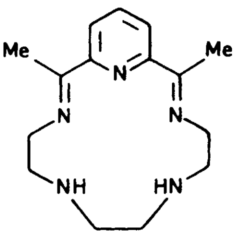
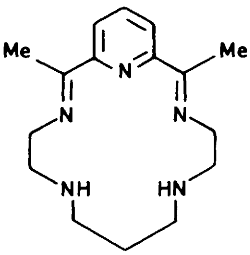
The complexes $[Fe^{II}L(CN)_2]\cdot xH_2O$ of the macrocyclic Schiff-base ligands L^1—L^3 derived from the condensation of 2,6-diacetylpyridine with 3,6-diazaoctane-1,8-diamine (L^1), 3,7-diazanonane-1,9-diamine (L^2), and 3,6-dioxaoctane-1,8-diamine (L^3) have been prepared and their magnetic susceptibilities and Mössbauer spectra studied over the temperature range 80—300 K. The complexes of the N_5 macrocycles L^1 and L^2 have low-spin (S = 0) ground states and are assigned six-co-ordinate structures in which the macrocycle acts as a quadridentate ligand with one secondary amine group unco-ordinated. This contrasts with the situation in all previously characterised complexes of these macrocycles (containing other metal ions and/or other axial ligands) where all five potential donor atoms are co-ordinated in a pentagonal planar arrangement. The exceptional structure of the present complexes is attributed to the ligand-field stabilization energy associated with the low-spin, approximately octahedral configuration generated by the strong field cyanide ligands. The magnetic properties of $[FeL^3(CN)_2]\cdot H_2O$ exhibit a complex variation with temperature. The thermodynamically stable forms are high-spin (S = 2) at ambient temperature and low-spin (S = 0) below 150 K while between 150 and 200 K the stable form appears to contain approximately equal numbers of high-spin and low-spin molecules. The structure of the low-spin form is believed to be six-co-ordinate, with one ether oxygen of the macrocycle unco-ordinated while the high-spin form may have either a six- or a seven-co-ordinate structure.

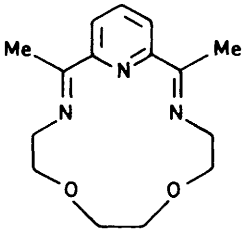
An interesting aspect of the structural chemistry of co-ordination compounds of multidentate ligands concerns the extent to which the co-ordination geometry is determined by metal-ion properties (size, electron configuration) as against properties of the ligand (preferred conformation, nature and disposition of donor atoms). Such questions arise in complexes of multidentate ligands of limited flexibility which often cannot respond freely to the varying stereochemical preferences of different metal ions. Examples of the interplay between opposing geometrical demands of metal ion and ligand are found among complexes of the potentially quinquedentate macrocyclic ligands L^1—L^3.[1] Thus, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, and Zn^{2+} are effective templates for the synthesis of pentagonal bipyramidal complexes (of the template metal ion) from 2,6-diacetylpyridine and the appropriate α,ω-diprimary amine. In all of these complexes the five donor atoms of the macrocycle comprise the pentagonal plane, the axial sites of the pentagonal bipyramid being occupied by unidentate anionic or solvent ligands.[1] In contrast, neither Ni^{2+} nor Cu^{2+} is effective as template for any of the macrocycle syntheses. This contrasting behaviour has been related[1] to the preference of the d^8 and d^9 ions for stereochemistries (octahedral, tetragonal, square pyramidal, square planar) in which the metal–ligand bonds are in an orthogonal relationship as is apparent from a comparison of the crystal-field stabilisation energies in fields of O_h and D_{5h} symmetry.[2] It is significant that while Ni^{II} will apparently not form an isolable complex of L^2, for example, an octahedral complex $[Ni(L^2 + ROH)(NCS)]^+$ (R = Me or Et) has been prepared and characterised. In this complex the new macrocycle (L^2 + ROH), derived from L^2 by addition of ROH across one azomethine bond, now has sufficient flexibility, denied to L^2 itself, to co-ordinate on five sites of an octahedron.[3]



L^1



L^2



L^3

In this paper we describe some low-spin Fe^{II} complexes of L^1—L^3 in which a different device is adopted so as to provide the metal ion with the six-co-ordinate environment required for an S = 0 ground state. One of the Fe^{II} complexes exhibits a thermally-controlled high-spin (S = 2) $\rightleftharpoons$ low-spin (S = 0) spin transition having unusual characteristics which are also described.

Table 1. Analytical, i.r., and electrical conductance data for the complexes

	Analysis (%)											
	Found			Calc.			I.r. bands/cm^{-1}			Λ*/S cm^2 mol^{-1}		
Complex	C	H	N	C	H	N	ν(NH)	ν(C=N)	ν(C≡N)	MeCN	$C_2H_4Cl_2$	H_2O
[FeL^1(CN)$_2$]·H_2O	51.0	6.3	24.7	51.1	6.3	24.6	3 300	1 620w	2 105, 2 098	41	6.0	39
[FeL^1(CN)$_2$]·0.5H_2O	52.3	6.2	25.2	52.3	6.2	25.1	3 320, 3 220	1 620w	2 105, 2 096	41	5.7	39
[FeL^2(CN)$_2$]	54.3	4.7	12.6	54.7	4.6	12.7	3 310	1 620w	2 105, 2 098	40	5.6	32
[FeL^3(CN)$_2$]·H_2O	50.6	5.7	17.7	50.9	5.8	17.5		1 640s	2 104	10	0.4	99

* 10^{-3} mol dm^{-3} solutions at 25 °C.

Experimental

2,6-Diacetylpyridine and 3,6-diazaoctane-1,8-diamine were used as supplied (Aldrich). 3,7-Diazanonane-1,9-diamine[4] and 3,6-dioxaoctane-1,8-diamine[5] were prepared by literature methods.

Preparation of the Complexes.—The same general method of preparation was used for the three complexes investigated. 2,6-Diacetylpyridine (3.26 g, 0.02 mol) and the appropriate diprimary amine (0.02 mol) were added to an O_2-free solution of $FeCl_2·4H_2O$ (4.0 g, 0.02 mol) in MeOH (200 cm^3) and H_2O (50 cm^3) containing $Na_2S_2O_4$ (2 g). The resulting deep blue-black solution was gently refluxed for 12—16 h under an atmosphere of N_2. The volume of the solution was reduced to about half under a stream of N_2 and then filtered under N_2 into a solution of NaCN (20 g) in O_2-free H_2O (100 cm^3) containing $Na_2S_2O_4$ (1 g). At this stage the colour changed from deep blue to deep blue-purple. The solution was further reduced in volume to *ca.* 100 cm^3 by passage of N_2 at 50 °C. It was then cooled in a ice-bath and filtered under N_2 to give the deep blue-purple microcrystalline product. This was washed with warm O_2-free H_2O to remove $Na_2S_2O_4$ and NaCN impurities and then with O_2-free MeOH. The product was dried *in vacuo*. Yields were in the range 30—45% in different preparations.

When the complex [FeL^1(CN)$_2$]·H_2O, obtained as above, was recrystallised from O_2-free ethanol, the hemihydrate [FeL^1(CN)$_2$]·0.5H_2O was obtained.

Physical Measurements.—I.r. spectra were measured as KBr discs and paraffin mulls in the range 4 000—250 cm^{-1} using a Perkin-Elmer 598 spectrometer. Electronic spectra were recorded between 35 000 and 10 000 cm^{-1} on a Unicam SP700 spectrophotometer. Electrical conductances of 10^{-3} mol dm^{-3} solutions were measured at 25 °C using a cell of cell constant 0.0368 constructed from bright platinum electrodes in conjunction with a resistance/capacitance bridge. Magnetic susceptibilities in the range 90—300 K were obtained by the Gouy method using a Newport Instruments variable-temperature magnetic balance. Initial Mössbauer spectra were obtained at 293 and *ca.* 80 K using a ^{57}Co in Pd source in conjunction with a Harwell constant acceleration spectrometer. Subsequent measurements using a spectrometer consisting of a constant acceleration electromechanical drive and a Nuclear Data ND 2400 multichannel analyser operating in the multiscaler mode. A 50-mCi source of ^{57}Co in rhodium was used, the calibration being effected with a metallic iron absorber. All velocity scales and isomer shifts are referred to the iron standard at 298 K. Full details have been reported previously.[6]

Results and Discussion

Analytical and selected physical data pertaining to the complexes are collected in Table 1. The deep blue or blue-purple complexes have long term stability in the solid state at ambient temperature but decompose at temperatures between 120 and 220 °C. Differential thermal analysis indicated distinct differences between [FeL^1(CN)$_2$]·H_2O and [FeL^1(CN)$_2$]·0.5H_2O. The hemihydrate is stable at temperatures up to *ca.* 200 °C after which the organic ligand begins to decompose. The monohydrate, however, starts to loose weight slowly at 120 °C and then more rapidly at *ca.* 150 °C. The complexes are soluble in water and in most organic solvents of moderate-to-high polarity. Solutions appear stable for long periods in the absence of O_2 but lose colour and become turbid in the presence of air.

Comparison of the i.r. spectra of the cyanide complexes with those of other structurally defined complexes[1,7,8] of the same macrocyclic ligands but containing other metal ions and/or other anionic ligands confirm the presence of the macrocycle and the absence of absorptions, *e.g.* ν(C=O) and ν(NH_2) due to the precursor ketone and primary amine. There are, however, some notable differences in the spectra. Thus, the ν(C=N) vibration, which in all previously investigated[1] complexes of these macrocyclic ligands occurs as a strong band at 1 630—1 660 cm^{-1}, now appears as a broad band of low intensity at 1 620 cm^{-1} except in the case of [FeL^3(CN)$_2$]·H_2O. The dramatic reduction in intensity of ν(C=N) in the L^1 and L^2 complexes can be related to their low-spin ($S = 0$) nature at room temperature (see later) this being a previously noted feature of the i.r. spectra of low-spin Fe^{II} complexes of imine ligands.[9] Spectra in the ν(NH) region of the L^1 and L^2 complexes were variable, [FeL^1(CN)$_2$]·H_2O and [FeL^2(CN)$_2$] showed a sharp medium-to-strong band around 3 310 cm^{-1} whereas [FeL^1(CN)$_2$]·0.5H_2O displayed two sharp bands at 3 320 and 3 220 cm^{-1}. The hydrated complexes showed one or two strong well defined absorption bands between 3 450 and 3 550 cm^{-1} as well as a strong broad absorption between 500 and 530 cm^{-1} which we assign to a rocking mode[10] of H_2O perhaps hydrogen bonded to unco-ordinated NH or ether groups (see later). All the complexes also exhibit a sharp band at *ca.* 2 100 cm^{-1} showing slight splitting attributable to ν(C≡N) of the CN$^-$ groups. The occurrence of ν(C≡N) at higher frequencies (*ca.* 2 100 cm^{-1}) than in ionic CN$^-$ (2 080 cm^{-1} in KCN)[10] is evidence for co-ordination of the CN$^-$ group in the complexes. In agreement with this conclusion the electrical conductances (Table 1) in H_2O, MeCN, and $C_2H_4Cl_2$, while indicating some ionic dissociation, are considerably lower than expected for uni-univalent electrolyte behaviour.[11] Moreover, electronic spectra in MeCN and $C_2H_4Cl_2$ are in fair agreement with those obtained for the solid complexes (Table 2), all showing two or three principal resolved features in the visible region. The high intensities indicate that the bands have a charge transfer, probably metal-to-ligand rather than a purely ligand-field origin. Spectra in H_2O are somewhat different from those of the solids or the solutions in the other solvents.

Final confirmation that the complexes contain the co-ordinated macrocycles (L^1, L^2, or L^3) was obtained by the

Table 2. Electronic spectra in solution for the complexes; band maxima (10^3 cm^{-1}) and ε (dm^3 mol^{-1} cm^{-1}) in parentheses

Complex	Solid	MeCN	$C_2H_4Cl_2$	H_2O
$[FeL^1(CN)_2]\cdot H_2O$	19.5, 16.2, 13.6	19.9 (4 800), 16.4 (1 200), 13.7 (sh)	19.9 (2 000), 15.9 (1 250), 13.7 (sh)	21.0 (3 500), 18.0 (1 200), 14.9 (250)
$[FeL^1(CN)_2]\cdot 0.5H_2O$	19.5, 16.1, 13.4	19.9 (4 900), 16.3 (1 200), 13.7 (sh)	19.8 (2 100), 15.9 (1 200), 13.8 (sh)	21.0 (3 200), 18.0 (1 150), 15.0 (sh)
$[FeL^2(CN)_2]$	19.7, 16.0, 13.2	19.8 (4 900), 16.1 (1 200), 13.2 (760)	19.6 (2 400), 15.9 (1 080), 13.3 (sh)	21.1 (4 700), 18.0 (1 260), 14.9 (sh)
$[FeL^3(CN)_2]\cdot H_2O$	19.2, 14.0	19.8 (2 580), 15.4 (1 880), 13.7 (sh)	19.8 (3 140), 15.2 (1 820), 13.7 (sh)	20.7 (1 080), 16.7 (1 320), 11.4 (sh)

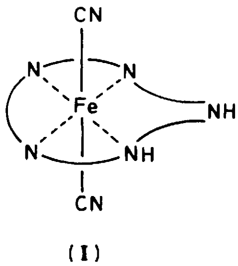
Table 3. Magnetic and Mössbauer data for the complexes

	$\mu_{eff.}$/B.M.[a]	δ[b]/mm s^{-1}	ΔE_Q/mm s^{-1}
$[FeL^1(CN)_2]\cdot H_2O$	0.44[b]	0.10[c]	0.32[c]
		0.16[d]	0.35[d]
$[FeL^1(CN)_2]\cdot 0.5H_2O$	0.38[c]	0.14[c]	0.44[c]
		0.20[d]	0.47[d]
$[FeL^2(CN)_2]$	0.70[c]	0.06[c]	0.20[c]
		0.16[c]	0.20[d]
$[FeL^3(CN)_2]\cdot H_2O$	5.09[c]	0.84[c]	3.18[c]
	3.58[e]	{0.87 0.22}[e]	{3.30 1.34}[e]
	1.02[f]		

[a] B.M. = 9.274×10^{-24} J T^{-1}. [b] Relative to iron foil. [c] 293 K. [d] 80 K. [e] 195 K, on slow cooling from 293 K. [f] 140 K, on slow warming after rapid quenching to 80 K.

successful isolation in good yield of the known complexes[7,8] $[FeL(NCS)_2]$ (L^1—L^3) by treatment of ethanolic solutions of the cyanide complexes with a large excess of NaNCS followed by concentration.

Magnetic Properties and Mössbauer Spectra.—The three complexes of the N_5 macrocycles L^1 and L^2 are virtually diamagnetic having room-temperature magnetic moments (Table 3) between 0.4 and 0.7 B.M., *i.e.* values appropriate to the small residual temperature-independent paramagnetism usually observed for low-spin Fe^{II} systems. The Mössbauer spectra (Table 3), measured at 293 and 80 K, consisted of one quadrupole split doublet having small isomer shifts (0—0.2 mm s^{-1}, relative to iron foil) and quadrupole splittings (0.2—0.5 mm s^{-1}) as expected for Fe^{II} with a spin singlet ground state.[12] The observation of a $S = 0$ ground state indicated by these two properties would appear to exclude the seven-co-ordinate (pentagonal bipyramidal) structure for these complexes, found previously[1,7] for other Fe^{II} complexes of the same macrocycles having other, weaker field, anionic ligands such as NCS^-. This is because spin singlet ground states are not possible for d^6 ions in D_{5h} symmetry. We conclude therefore that the complexes have six-co-ordinate, approximately octahedral, structures. Since both CN^- groups appear to be co-ordinated, probably in a *trans* relationship because of the smallness of the splitting in ν(C≡N), it follows that L^1 and L^2 must be co-ordinated equatorially in a quadridentate rather than a quinquedentate fashion, *i.e.* one of the five potential nitrogen atoms is excluded from the co-ordination sphere [structure (**I**)]. In view of the nature of the macrocyclic ligands, containing a planar conjugated trimethine segment and a flexible saturated polymethylenediaza segment, there can be little doubt that the unattached donor is one of the two secondary amine groups. Inspection of molecular models confirms that such an arrangement is the only one possible for a quadridentate co-ordination mode, even this involving some bond-angle strain within the macrocycle. The models further indicate that if one NH group is not co-ordinated in the equatorial plane there is insufficient flexibility for it to occupy an axial site as would be possible in larger macrocycles of the same class.[3]



(**I**)

In contrast to the cyanide complexes of the N_5 macrocycles L^1 and L^2, the complex $[FeL^3(CN)_2]\cdot H_2O$ of the N_3O_2 macrocycle is high-spin at ambient temperature. This is apparent not only from the magnetic properties ($\mu_{eff.}$ = 5.09 B.M. at 293 K) but also from the Mössbauer spectrum which at 293 K shows a single quadrupole split doublet with an isomer shift (δ) of 0.84 mm s^{-1} (relative to iron foil) and a quadrupole splitting (ΔE_Q) of 3.18 mm s^{-1}. These values of δ and ΔE_Q clearly define the metal atoms as having an $S = 2$ configuration.[12] When the complex (specimen A) was slowly cooled (*i.e.* at a cooling rate of *ca.* 2° min^{-1}) the magnetic moment remained essentially constant down to *ca.* 225 K at which point a fairly abrupt decrease in moment was observed (curve A in Figure 1) levelling out at 3.58 B.M. at temperatures below *ca.* 210 K. Further cooling down to 90 K caused no significant further decrease in moment. On subsequent warming of the complex to room temperature the moment started to increase at *ca.* 220 K levelling out at a value of 5.09 B.M. above *ca.* 240 K. As may be seen in Figure 1 the rate of increase in moment on warming is less abrupt than the decrease on cooling. There is also a pronounced hysteresis loop.

The observation of a magnetic moment of ~3.6 B.M. at low temperature at first suggested a spin transition to a spin triplet ($S = 1$) ground state. However, Mössbauer spectra at 80 K clearly ruled this out. The spectrum at this temperature consisted of two quadrupole split doublets of comparable relative intensity, one having δ and ΔE_Q of 0.87 and 3.30 mm s^{-1} and the other δ = 0.22 and ΔE_Q = 1.34 mm s^{-1}. The first of these doublets has characteristics very similar to those observed at room temperature and is clearly due to a high-spin ($S = 2$) component. Taking into account the magnetic properties it follows that the second (inner) doublet must arise from a fully low-spin ($S = 0$) component.

Confirmation for the occurrence of a spin singlet component at low temperature was obtained when a second sample (specimen B, from a different preparation) of the complex was rapidly quenched in liquid nitrogen and the magnetic properties investigated as the specimen was slowly warmed from 100 K to room temperature. It was found that below 130 K the moment

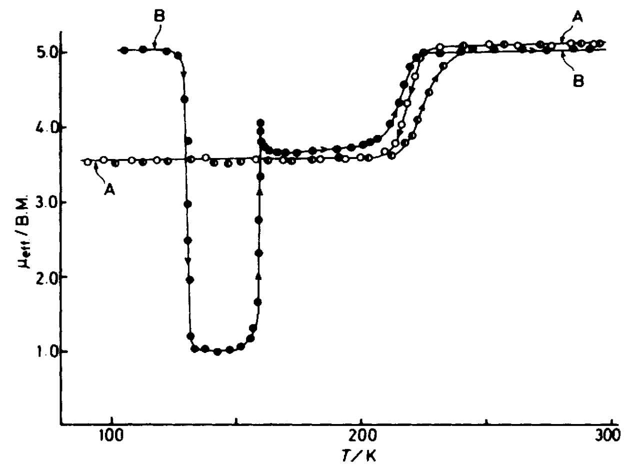


Figure 1. Variation of magnetic moment of $[FeL^3(CN)_2]\cdot H_2O$ with temperature. Curve A, specimen A on descending temperature (○) and ascending temperature (◐). Curve B, (●) specimen B on slow warming following rapid quenching to 80 K

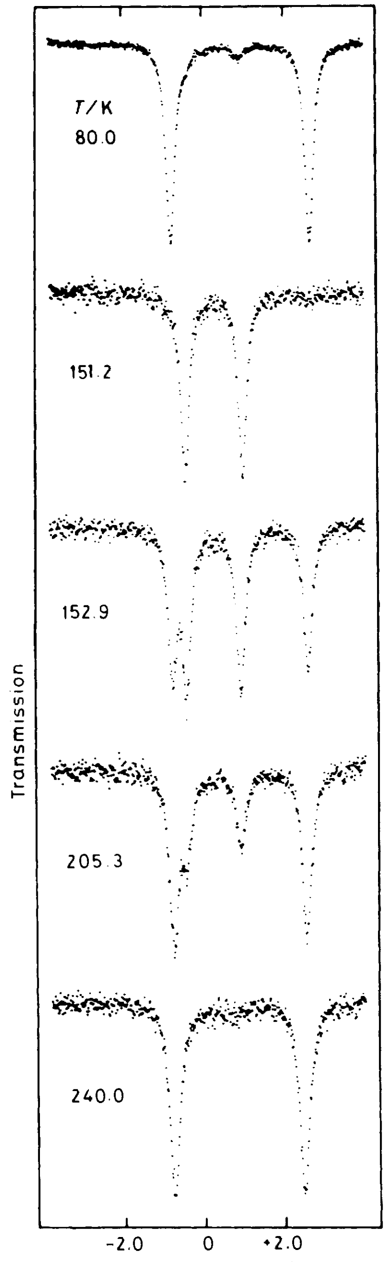
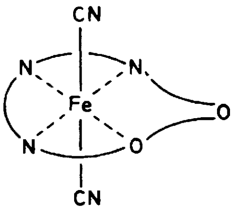


Figure 2. ^{57}Fe Mössbauer spectra for a rapidly quenched (to 80 K) sample of $[FeL^3(CN)_2]\cdot H_2O$ and for the process of its slow warming to room temperature

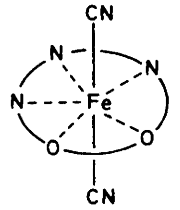
was 5.0 B.M. showing that the $S = 2$ state has been 'frozen-in' by the rapid quenching. As the sample was slowly warmed from 110 K (at an initial rate of *ca.* 0.5° min^{-1}) the moment was observed to fall to ~ 1.0 B.M. at *ca.* 130 K (curve B in Figure 1). Although the decrease in $\mu_{eff.}$ was abrupt in terms of temperature variation, being 90% complete over a temperature interval of *ca.* 5°, the transition was very slow requiring *ca.* 2 h for completion. The magnetic moment remained close to 1.0 B.M. on further slow increase in temperature to ~ 150 K demonstrating that under these conditions a near complete conversion to the singlet state had been achieved. Above 150 K the magnetic moment started to rise, levelling out at *ca.* 3.65 B.M. above 160 K. This increase in paramagnetism was also abrupt with respect to temperature but again rather slow in terms of time, taking up to 45 min for completion at 160 K. An interesting feature of this transition was the 'overshoot' seen in Figure 1 in which the moment reached a maximum value of ~ 4.0 B.M. before falling to a steady value of 3.65 B.M. On further rise in temperature the moment remained fairly constant until *ca.* 190 K at which point a further increase to $\mu_{eff.} = 5.01$ B.M. occurred (Figure 1) as observed for specimen A but over a somewhat lower range of temperatures.

A repetition of the cycle of temperature changes on the same specimen B, *i.e.* rapid quenching to 80 K followed by slow heating to room temperature, produced much the same response in magnetic properties as described above and illustrated in Figure 1 for the first cycle, though with minor variations in the temperature of onset of the various transitions and in the rates with which they took place. However, in a third experiment on the same specimen in which the temperature was decreased moderately slowly (*ca.* 2° min^{-1}) from room temperature to 95 K the magnetic moment remained at the high-spin value of ~ 5.0 B.M. and did not exhibit the 5.0 to 3.6 B.M. transition between 230 and 200 K observed when specimen A was treated in the same way; however, on subsequent slow warming from 95 K the same pattern of changes in magnetism shown by the other samples (see curve B, Figure 1) was observed. It thus appears that the precise magnetic behaviour is dependent on pre-history and/or sample preparation.

The observations relating to the magnetic properties of $[FeL^3(CN)_2]\cdot H_2O$ (specimen B) following rapid quenching to 80 K were confirmed by the study of the ^{57}Fe Mössbauer effect on another sample of the same preparation. A number of representative spectra are displayed in Figure 2. Thus, rapid quenching of the sample from room temperature to 80 K produced a doublet having $\Delta E_Q = 3.45$ mm s^{-1} and $\delta = 0.95$ mm s^{-1}, values which are characteristic for the high-spin component of the substance. The high-spin fraction (n_{HS}) has been estimated from the Mössbauer effect areas to be 0.96 (the low-intensity line in the centre of the spectrum at 80 K is due to the small contribution by the low-spin component). If the sample is slowly warmed up, the spectrum is transformed in the region of 130 K to another doublet having, at 151.2 K, $\Delta E_Q = 1.43$ and $\delta = 0.28$ mm s^{-1}, values which are typical of the low-spin component and here $n_{HS} = 0$. With further warming, a small high-spin component shows up at 152.5 K ($n_{HS} = 0.24$), its intensity rising to $n_{HS} = 0.57$ at 152.9 K. Here, we found for



(II)



(III)

the high-spin doublet $\Delta E_Q = 3.36$ and $\delta = 0.91$ mm s^{-1}, whereas for the low-spin doublet $\Delta E_Q = 1.34$ and $\delta = 0.25$ mm s^{-1} were obtained. The value of n_{HS} remains unchanged up to *ca.* 180 K where a gradual conversion of the remaining low-spin fraction to the high-spin state sets in, see for example the intermediate spectrum at 205.3 K. Finally, the transition is completed at *ca.* 218 K. At 240.0 K, we observed, for the pure high-spin state ($n_{HS} = 1.0$), $\Delta E_Q = 3.22$ and $\delta = 0.86$ mm s^{-1} in excellent agreement with the initial values. It should be noted that the final conversion to the high-spin state above 180 K takes place in a somewhat lower temperature region than that of the original hysteresis curve, see Figure 1.

Conclusions

The results show that the $[FeL(CN)_2]\cdot xH_2O$ complexes have $S = 0$ ground states at ambient temperature for the case of the two N_5 macrocycles ($L = L^1$ or L^2). Since a spin singlet ground state is precluded in D_{5h} symmetry it must be concluded that these complexes have six-co-ordinate, approximately octahedral, structures in which one secondary amine group is not co-ordinated to the metal. This contrasts with all previously determined structures[1,7] of metal complexes of these two macrocycles both of which are well suited to co-ordinate in an approximately planar pentagonal mode. The exceptional behaviour observed here can be related to the large crystal-field stabilisation energy (c.f.s.e.) associated with the fully spin-paired d^6 configuration in O_h symmetry engendered by the presence of two high-field CN^- ligands together with four macrocyclic nitrogen donors. Clearly, the c.f.s.e. effects are large enough to overcome the effects of macrocycle strain accompanying the quadridentate co-ordination mode.

The behaviour of the complex $[FeL^3(CN)_2]\cdot H_2O$ containing the N_3O_2 macrocycle is most unusual. The results show that at temperatures below 150 K the thermodynamically stable form is a spin singlet. For the same reasons advanced above we conclude that the structure of this low-temperature form is, like those of the L^1 and L^2 complexes, six-co-ordinate with one unco-ordinated ether oxygen. At higher temperatures, between *ca.* 160 and 200 K, the stable form of the complex appears to be one in which the low-spin ($S = 0$) and high-spin ($S = 2$) forms co-exist in an approximate 1 : 1 ratio. At yet higher temperatures (above 230 K) the complex exists entirely in the quintet form.

The question arises—what is the structure of the high-spin ($S = 2$) form of the complex? There are two possibilities. The complex could be six-co-ordinate [structure **(II)**] as in the low-temperature form or it could have a seven-co-ordinate, pentagonal bipyramidal, structure **(III)** as in complexes such as $[FeL^3(NCS)_2]$ containing other anionic ligands.[7] A gross change in structure, as from six- to seven-co-ordinate, would be unusual in the solid state but would be consistent with the apparent need for lattice reorganization accompanying the spin change as reflected in the hysteresis effects and the 'freezing-in' of the high-spin form on rapid quenching. Moreover, the c.f.s.e. effects associated with the low-spin configuration and presumed to be responsible for the adoption of the six-co-ordinate structure at low temperature are absent at room temperature. However, on presently available information it does not seem possible to decide between alternatives **(II)** and **(III)**. Unfortunately, single crystals of suitable quality for *X*-ray analysis have not been obtained.

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