Electron Spin Resonance Spectroscopy of some Dianiono(1,4,8,11-tetra-azacyclotetradecane)-iron(III) and -nickel(III) Salts

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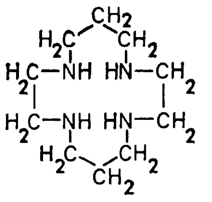
The complexes *trans*-$[NiX_2L][ClO_4]$ [X = Cl or Br; L = 1,4,8,11-tetra-azacyclotetradecane (cyclam)] are shown to dissociate in solution according to the equilibrium $[NiX_2L]^+ \rightleftharpoons [NiXL]^{2+} + X^- \rightleftharpoons [NiL]^{3+} + 2\,X^-$. The e.s.r. spectrum of each species has been recorded and analysed. The unpaired electron is in an orbital which is mainly $3d_{z^2}$ with significant delocalisation on to a *p* orbital on each halogen. The e.s.r. spectra of *trans*-$[FeCl_2L][ClO_4]$ and *trans*-$[Fe(NCS)_2L][NCS]$ have *g ca.* 3.2, 2.2, and 1.1, and show that the ground state is $^2T_2(t_{2g}{}^5)$, but the spectrum of *trans*-$[FeBr_2L][ClO_4]$ exhibits additional lines at $g_\parallel = 2$ and $g_\perp = 6$, showing the presence of a high-spin–low-spin equilibrium with *ca.* 71% low spin at 293 K.

THE structure and bonding in transition-metal complexes of nitrogen-bonded aromatic macrocyclic ring systems has been well studied by many spectroscopic techniques including electron spin resonance. Less attention has been paid to analogous aliphatic complexes, although much is known about simple amine complexes. Recently,[1] the complex cations *trans*-$[MX_2L]^+$ have been prepared [L = 1,4,8,11-tetra-azacyclotetradecane (cyclam); M = Fe^{III}, X = Cl, Br, or NCS; M = Ni^{III}, X = Cl or Br]; the counter anion may be $[ClO_4]^-$ or $[NCS]^-$. Their magnetic susceptibility suggests one unpaired electron, indicating a low-spin d^5 or d^7 configuration except for *trans*-$[FeBr_2L][ClO_4]$ where $\mu_{eff.} = 3.90$ and a high-spin–low-spin equilibrium seems probable. We have made e.s.r. measurements on each complex and confirm these assignments.



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EXPERIMENTAL

All the complexes were prepared according to the published procedures.[1] E.s.r. spectra were measured on a Varian E-3 spectrometer at 77 K and varying temperatures up to room temperature. The solvent used for each was dimethyl sulphoxide. In order to prevent dissociation of $[NiBr_2L][ClO_4]$, some concentrated hydrobromic acid was added to the solution.

RESULTS AND DISCUSSION

trans-$[NiBr_2L][ClO_4]$.—The spectrum at 77 K shows axial symmetry with the parallel feature split into seven almost equally spaced lines of relative intensity *ca.* 1 : 2 : 3 : 4 : 3 : 2 : 1. There were also seven lines centred about $g_\perp$, but these are less well resolved because of overlap of lines with the low-field parallel features. The spectrum is shown in Figure 1(*a*). A complication arises because of the two Br isotopes: ^{79}Br, $I = \frac{3}{2}$, $\mu = 2.099\,1$, 50.6%; ^{81}Br, $I = \frac{3}{2}$, $\mu = 2.262\,6$, 49.4%. Nickel has no isotopes with a nuclear spin in sufficient natural abundance to cause further splitting. The distribution of isotopes in the molecule is such that there is *ca.* 25% each of $^{79}Br–Ni–^{79}Br$ and $^{81}Br–Ni–^{81}Br$, and *ca.* 50% of $^{79}Br–Ni–^{81}Br$. The three types of spectra are shown in Figure 2 together with the accumulated spectrum. The two shoulders present in the lowest-field parallel hyperfine line (m_I +3) can be explained by the different contributions of the two Br isotopes. The spin-Hamiltonian parameters are given in the Table.

The unpaired electron is primarily in an $a_{1g}(d_{z^2})$ orbital because $g_\perp > g_\parallel \sim 2$. Had the electron been in a $b_{1g}(d_{x^2-y^2})$ orbital (in D_{4h} symmetry), then $g_\parallel > g_\perp > 2$. Furthermore, analysis of the Br hyperfine tensor, using the average value for the two Br isotopes, *viz.* $A_\parallel$ = 137 G and $A_\perp$ = 39 G and assuming both to be positive, gives $A_{iso.}$ = 72 G and $A_{aniso.}$ = 65 G. From these, the 4*s* and 4*p* character of the unpaired electron in its interaction with Br is deduced using the weighted value of 8 067 G for the electron entirely in a 4*s* orbital on Br and 477 G for the electron entirely in a 4*p* orbital.[2] The

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[1] P. K. Chan and C. K. Poon, *J.C.S. Dalton*, 1976, 858.

[2] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

deduced 4*s* and 4*p* characters are 0.9 and 13.6%. These large values support the notion of the electron in an a_1 orbital. Alternative combinations of signs for the Br hyperfine tensor yield meaningless or improbable results.

Experimental spin-Hamiltonian parameters*

	g_z	g_x	g_y	g_{av}	$g_{iso.}$	A_z/G	A_x/G	A_y/G	A_{av}/G	$A_{iso.}$/G
$[Ni^{III}Br_2(cyclam)]^+$	2.014	2.170	2.170	2.121		137	39	39	72	
$[Ni^{III}Br(cyclam)]^{2+}$	2.060				2.173	150				53
$[Ni^{III}Cl_2(cyclam)]^+$	2.022	2.180	2.180	2.127		28	<5	<5	<9	
$[Ni^{III}Cl(cyclam)]^{2+}$	2.071	2.136	2.182	2.130	2.127					
$[Ni^{III}(cyclam)]^{3+}$	2.026	2.242	2.242	2.170	2.169					
$[Fe^{III}Cl_2(cyclam)]^+$	3.26	2.23	1.15							
$[Fe^{III}(NCS)_2(cyclam)]^+$	3.20	2.23	1.03							
$[Fe^{III}Br_2(cyclam)]^+$ low spin	3.25	2.34	1.08							
$[FeBr_2(cyclam)]^+$ high spin	2	6	6							

$$A_{av} = \tfrac{1}{3}(A_x + A_y + A_z),\ g_{av} = \tfrac{1}{3}(g_x + g_y + g_z).$$

* Throughout this paper: 1 G = 10^{-4} T.

The e.s.r. spectrum measured at room temperature shows four equally spaced lines 53 G apart and of the same intensity. This spectrum is attributed to a species in solution with one Br atom and suggests that the dissociative equilibrium (1) occurs.

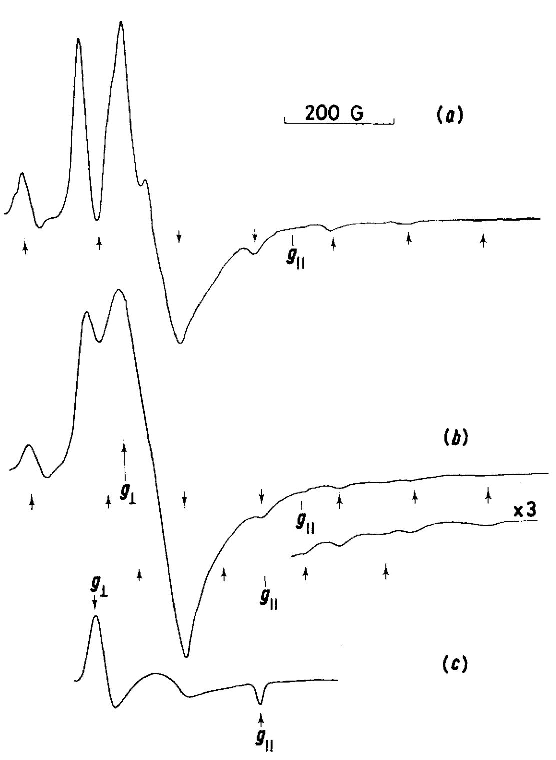

FIGURE 1 E.s.r. spectra at 77 K of solutions containing: (*a*) $[NiBr_2L]^+$ (the arrows show the seven parallel features); (*b*) a mixture of $[NiBr_2L]^+$ and $[NiBrL]^{2+}$ (the group of seven arrows shows the parallel features of $[NiBr_2L]^+$ and the group of four arrows the parallel features of $[NiBrL]^{2+}$; and (*c*) $[NiL]^{3+}$

$$[NiBr_2L]^+ \rightleftharpoons [NiBrL]^{2+} + Br^- \qquad (1)$$

In the absence of HBr, the spectrum of the frozen solution shows additional features [Figure 1(*b*)]. These comprise four lines at high field with a spacing of 150 G which are attributed to hyperfine coupling to a single bromine atom. The remainder of the spectrum differs from that of the dibromo-complex, but is dominated by the latter such that the parameters cannot easily be determined, although there is evidence for the splitting of the perpendicular feature.

After addition of silver(I) perchlorate to the solution of $[NiBr_2L]^+$ the spectrum at 77 K showed axial symmetry with no hyperfine coupling [Figure 1(*c*)]. This spectrum is attributed to the cation $[NiL]^{3+}$ with both bromine atoms removed and possibly replaced by weakly interacting solvent molecules. The overall equilibrium may be described as (2).

$$[NiX_2L]^+ \underset{HX}{\overset{Ag[ClO_4]}{\rightleftharpoons}} [NiXL]^{2+} + X^- \underset{HX}{\overset{Ag[ClO_4]}{\rightleftharpoons}} [NiL]^{3+} + 2X^- \qquad (2)$$

trans-$[NiCl_2L][ClO_4]$.—The spectrum of the dichloro-complex at 77 K shows very clear axial symmetry with the parallel feature split into seven equally spaced lines (28 G) with relative intensity 1 : 2 : 3 : 4 : 3 : 2 : 1 [see Figure 3(*a*)]. The perpendicular feature is sharp and shows no evidence of hyperfine coupling. Any coupling to chlorine must be very small (<5 G). There are two isotopes of chlorine: ^{35}Cl, $I = \frac{3}{2}$, $\mu = 0.820\,9$, 75.4%; ^{37}Cl, $I = \frac{3}{2}$, $\mu = 0.683\,3$, 24.6%. We were not able to detect lines from the two isotopes, as was possible for the dibromo-complex. In fluid solution at room temperature, only a single broad line was detected suggesting that any hyperfine coupling is small (<10 G). The *g* values are similar to that for the dibromo-complex suggesting the same ground state, $a_{1g}(d_{z^2})$. Using the estimates for $A_{\perp}$ and $A_{iso.}$, then the chlorine 3*s* and 3*p* character of the unpaired electron is *ca.* 0.6 and 19%

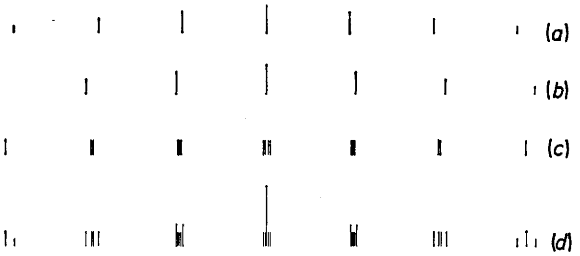

FIGURE 2 E.s.r. stick spectrum expected from the interaction of an unpaired electron with two equivalent Br atoms, showing the lines attributable to the two isotopes ^{79}Br and ^{81}Br in the combinations (*a*) ^{79}Br–^{79}Br, (*b*) ^{81}Br–^{81}Br, and (*c*) ^{79}Br–^{81}Br; (*d*) shows the total spectrum

respectively, taking the 100% values for 3*s* and 3*p* on chlorine (weighted) as 1 617 and 98 G respectively. The chlorine-electron population is rather greater than that for the dibromo-complex. This compares with 1 and 11% 3*s* and 3*p* character respectively for the unpaired electron in *trans*-$[Rh(CN)_4Cl_2]$ in KCl,[3] 1.0 and 17.5% for the corresponding nickel(III) complex,[4,5] 0.6 and 5.7% for the corresponding cobalt(II) complex,[5] and 0.6 and 3.2% for the corresponding iron(I) complex.[5,6] The large increase on going from Fe^I to Co^{II} to Ni^{III} is due to the progressively increasing positive charge on the metal drawing the Cl^- towards it. The smaller delocalisation with the rhodium(II) complex and with our dibromo-complex reflects the larger size of these atoms. It is satisfying that the delocalisation in *trans*-$[NiCl_2L]^+$ is very close to that found in *trans*-$[Ni(CN)_4Cl_2]^{3-}$.

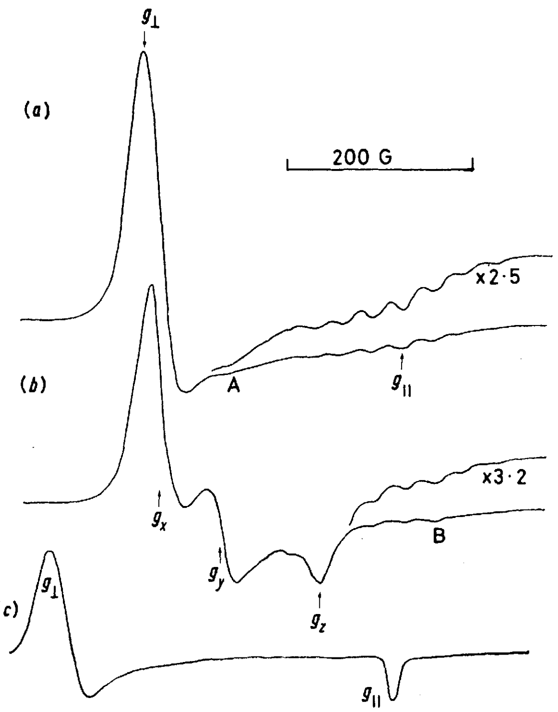

FIGURE 3 E.s.r. spectrum at 77 K of solutions containing (*a*) $[NiCl_2L]^+$, (*b*) a mixture of $[NiCl_2L]^+$ and $[NiClL]^{2+}$, and (*c*) $[NiL]^{3+}$

The possibility of a dissociative equilibrium was tested by addition of $Ag[ClO_4]$. The addition of a small amount, followed by rapid freezing, furnished the spectrum shown in Figure 3(*b*). The remnants of some of the dichloro-complex are seen at B in the Figure, but new features are seen labelled g_z and g_y, together with that labelled g_x (shifted slightly upfield compared with the $g_\perp$ of the dichloro-complex). A trace amount of the g_y feature of the monochloro-complex is seen in the spectrum of the dichloro-complex showing that some dissociation had taken place. The spectrum is assigned to the monochloro-complex because further addition of $Ag[ClO_4]$ yields the spectrum shown in Figure 3(*c*) which is identical to the spectrum of the solution of the dibromo-complex to which has been added excess of $Ag[ClO_4]$ [Figure 1(*c*)]. This spectrum is attributed to the complex ion $[NiL]^{3+}$.

The Symmetry of the Nickel Complexes.—Although the point-group symmetry of $[NiX_2L]^+$ is C_i,[7] as far as the nickel is concerned the four nitrogens are equivalent, each being approximately sp^3 hybridised and each is bonded to three carbon atoms. Thus the local symmetry is D_{4h}, and this is confirmed by the observed axial symmetry of the e.s.r. spectrum of the dichloro- and the dibromo-complexes. The same is true of $[NiL]^{3+}$, where the loss of two halides does not alter the symmetry about the nitrogen, although it affects the energy levels since the values of *g* are shifted. The small increase in $g_\parallel$ on going from the dibromo- to the dichloro-complex may arise from some destabilisation of the e_g orbitals by changes in the extensive π bonding. More important, however, is the stabilisation of $d_{z^2}(a_{1g})$ on removal of the two halides with consequent greater spin–orbit coupling of the a_{1g} and e_g orbitals which will increase $g_\perp$. The small changes in $g_\parallel$ arise from second-order effects and are too small to quantify.

The change to a lower symmetry having three *g* values is unambiguously seen in the monochloro-complex, where the lowest *g* value is increased to 2.071 in $[NiClL]^{2+}$. We suggest there has been a major change in the stereochemistry such that the nickel is surrounded by five ligands disposed approximately at the corners of a trigonal bipyramid. A consequence of this is that the order of the energy levels changes such that the unpaired electron is in a $d_{x^2-y^2}$ orbital. The symmetry in reality is probably much lower, and the orbital notation is arbitrary.

trans-$[FeCl_2L][ClO_4]$ *and trans*-$[Fe(NCS)_2L][NCS]$.—The spectra of frozen solutions at 77 K of both complexes are similar and easily interpreted in terms of a low-spin d^5 system with rhombic symmetry having a $^2T_2(t_{2g}{}^5)$ ground state. The *g* values are *ca.* 3.2, 2.2, and 1.1 for each (see Table) and the spectra are shown in Figure 4. There was no evidence for any hyperfine coupling. The theory of this ground state has been developed by Griffith[8] and extended by Harris.[9] The six $^2T_2$ states interact between themselves through spin–orbit coupling and the rhombic distortion to form two sets of three interacting states which split into three Kramer's doublets. The three interacting states have wavefunctions Φ_1, Φ_2, and Φ_3 and the energy of each is given by the interaction matrix, there being one matrix for one electron spin and an identical one for the other electron spin. A solution of this is $\psi_i = A_i\phi_1 +$

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[3] R. P. A. Muniz, N. V. Vugman, and J. Danon, *J. Chem. Phys.*, 1971, **54**, 1284.

[4] S. I. Zanette, A. O. Caride, and J. Danon, *J. Chem. Phys.*, 1976, **64**, 3381.

[5] S. C. Jain, K. V. Reddy, and T. R. Reddy, *J. Chem. Phys.*, 1975, **62**, 4366.

[6] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Dalton*, 1973, 14.

[7] B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.

[8] J. S. Griffith, *Mol. Phys.*, 1971, **21**, 135.

[9] G. M. Harris Loew, *Biophys. J.*, 1970, **10**, 196.

$B_i\phi_2 + C_i\phi_3$. μ is a measure of the difference in bonding perturbation of the four in-plane nitrogen atoms and the two axial ligands, *i.e.* the energy gap between the average of d_{xy} and d_{yz}, and d_{xy}, R is a measure of the rhombic distortion, *i.e.* the energy gap between d_{xz} and d_{yz}, and ζ is the spin–orbit coupling constant.[9]

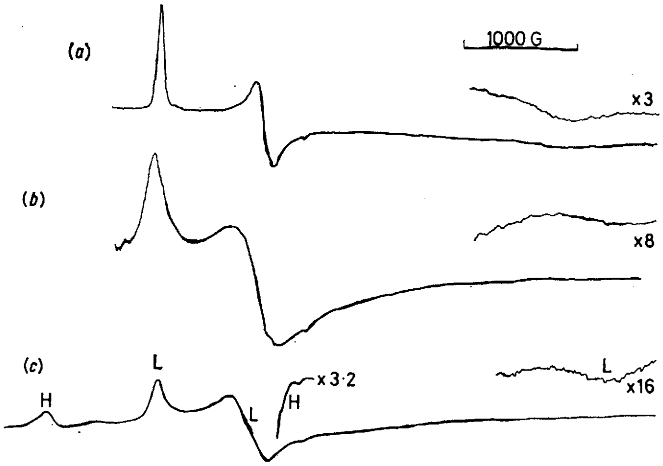

FIGURE 4 E.s.r. spectrum at 77 K of solutions containing (*a*) $[FeCl_2L]^+$, (*b*) $[Fe(NCS)_2L]^+$, and (*c*) $[FeBr_2L]^+$

$$\begin{array}{c|ccc}
 & \Phi_1 & \Phi_2 & \Phi_3 \\
\hline
\Phi_1 & -\frac{\zeta}{2} - E & \frac{\zeta}{\sqrt{2}} & \frac{R}{2} \\
\Phi_2 & \frac{\zeta}{\sqrt{2}} & \mu - E & 0 \\
\Phi_3 & \frac{R}{2} & 0 & \frac{\zeta}{2} - E
\end{array} \qquad (3)$$

In a magnetic field, each of the Kramer's doublets is split, but the only observed transition is in the lowest doublet. From first-order interaction of these states with the magnetic field, we obtain expressions (4)—(6) for the g values, where α, β, and γ are the coefficients of

$$g_x = 2[2\alpha\beta + \beta^2 - 2^{\frac{1}{2}}k\beta(\alpha + \gamma)] \qquad (4)$$

$$g_y = 2[-2\alpha\gamma + \beta^2 - 2^{\frac{1}{2}}k\beta(\alpha - \gamma)] \qquad (5)$$

$$g_z = 2[\alpha^2 - \beta^2 + \gamma^2 + k(\alpha^2 - \gamma^2)] \qquad (6)$$

ψ_i, and k is the orbital-reduction factor. Equation (7)

$$\alpha^2 + \beta^2 + \gamma^2 = 1 \qquad (7)$$

is also applicable. By substituting our experimental g values into equations (4)—(7), we can find α, β, γ, and k and then solve the interaction matrix for ζ/μ and R/μ.

Because of electron delocalisation, $k \neq 1$, and a value of $k < 1$ is expected. However, it is easily demonstrable[8] that for $S > 16$, where $S = g_x^2 + g_y^2 + g_z^2$, there is not a real solution of equations (4)—(6) for $k \leqslant 1$. This contradiction can be overcome by assuming that there are low-lying excited states which can mix with the $^2T_{2g}(^2t_{2g}^5)$ ground state leading to a substantial increase in the effective orbital angular momentum of the ground state. Griffith[8] showed that (for the first-row transition metals) this can be achieved by mixing with the $^4E_g(t_{2g}^4e_g^1)$ state, and now we obtain equations (8)—(10). Here k_1 and k_2 are the orbital-reduction

$$k = k_1 + 6Bk_2(a_1E_1^{-1} + a_2E_2^{-1}) \qquad (8)$$

$$E_1 = 10Dq + (7 - 34^{\frac{1}{2}})B - C \qquad (9)$$

$$E_2 = 10Dq + (7 + 34^{\frac{1}{2}})B - C \qquad (10)$$

factors associated with the t_{2g}^5 orbitals and $t_{2g}^4e_g^1$ orbital set respectively. $10Dq$ is the orbital splitting parameter, B and C are the Racah parameters, and a_1 and a_2 have the values -0.2 and 2.2 respectively.[8]

Unfortunately it is not easy to solve equations (8)—(10) mainly because of the different delocalisation of the d_{xz}, d_{yz}, and d_{xy} orbitals. However, the equations show that it *is* possible to have $k > 1$. For our system, we obtained a best-fit of solutions to fit our experimental g values, namely $k = 1.1$, $A = 0.90$, $B = -0.19$, and $C = -0.40$, from which it follows [equation (3)] that $\zeta/\mu = 0.4$ and $R/\mu = 0.5$. Taking a value of 400 cm^{-1} for ζ(Fe), we have $\mu = 1\,000$ cm^{-1} and $R = 500$ cm^{-1}. Comparing our results with those of Harris[9] for a range of six-co-ordinate iron complexes, we see that ours fall into the moderate-tetragonal–moderate-rhombic region like all the haem derivatives.

The positive value of μ implies that the axial are weaker than the equatorial ligands, and that the d_{xy} orbital is lower in energy than the d_{xz} and d_{xy}, and this is also expected for Ni^{III}. This allows us to explain the rhombic g symmetry of the low-spin form of Fe^{III}. In D_{4h} there will be a Jahn–Teller distortion to remove the degeneracy of the e_g^3 electrons.

trans-$[FeBr_2L][ClO_4]$.—The e.s.r. spectrum of frozen solutions of this complex showed quite different features [Figure 4(*c*)]. Three peaks at *g ca.* 3.25, 2.34, and 1.08 were similar to those found in the dichloro- and dithiocyanato-complexes. However, two further absorptions at $g_{\parallel} = 2$ and $g_{\perp} = 6$ with axial symmetry are seen, and are typical of the high-spin $A_1(t_{2g}^3,e_g^2)$ state. The relative intensity of the spectra for the high-spin and low-spin forms was temperature dependent, with the spectrum of the high-spin form decreasing in intensity with decreasing temperature. The complex is in an equilibrium between high- and low-spin states, a phenomenon which has been found in numerous other iron(III) complexes, *e.g.* ferrihemoprotein derivatives. For our complexes, the order of axial ligand-field strength is $[NCS]^- > Cl^- > Br^-$. The relative abundance of the two states can be deduced from the effective magnetic moment $\mu_{eff.}$ at room temperature by equation (11). Taking $\mu_L = 2.71$ (for the dichloro-complex) and

$$\mu_{eff.}^2 = \alpha\mu_L^2 + (1 - \alpha)\mu_H^2 \qquad (11)$$

$\mu_H = 5.92$ (for the $S = \frac{5}{2}$ state), we find that $\alpha = 0.71$ at 293 K.

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