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#### Donor Atom Set and Spin State of Iron(II). Bis(ligand)iron(II) and Bis(ligand)nickel(II) Complexes of 2,2'-Bipyridine-6-carbothioamide and 2,2'-Bipyridine-6-carboxamide

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2,2'-Bipyridine-6-carbothioamide (bpytm) and 2,2'-bipyridine-6-carboxamide (bpyam) are NNS and NNO donors, respectively, in their cationic bis(ligand)iron(II) and bis(ligand)nickel(II) complexes. The former ligand provides the stronger field and salts of  $[Fe(bpytm)_2]^{2+}$  have a singlet ground state, while those of  $[Fe(bpyam)_2]^{2+}$  have a quintet ground state. The magnetism and the electronic and Mössbauer spectra of salts of these cations have been measured. The low-temperature Mössbauer spectra of iron(II) complex salts of the carboxamide indicate, for the perchlorate and triflate salts, but not for the fluoroborate salt, a partial transition to singlet-state species. The mode of coordination of the ligands is indicated by infrared spectral data and has been confirmed by determination of the structures of [Ni(bpytm)<sub>2</sub>] Cl<sub>2</sub>.4H<sub>2</sub>O, [Ni(bpyam)<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O and [Fe(bpyam)<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub>. In addition, the structures of the free ligands have been determined. Hydrogen bonding is present in the free ligands and their complexes. 2,2'-Bipyridine-6-carbothioamide: monoclinic, space group  $P 2_1/c$ ,  $a \ 8.265(3)$ , b $11 \cdot 175(2)$ ,  $c \ 11 \cdot 114(4)$  Å,  $\beta \ 94 \cdot 47(2)^{\circ}$ ,  $Z \ 4. \ 2,2'$ -Bipyridine-6-carboxamide: monoclinic, space group  $P 2_1/c, a 13.581(2), b 9.926(1), c 16.824(3) \text{\AA}, \beta 116.481(7)^{\circ}, Z 8. [Ni(bpytm)_2] Cl_2.4H_2O: triclinic,$ space group  $P\bar{1}$ ,  $a 9 \cdot 291(5)$ ,  $b 12 \cdot 426(7)$ ,  $c 13 \cdot 425(7)$  Å,  $\alpha 113 \cdot 54(3)$ ,  $\beta 95 \cdot 63(3)$ ,  $\gamma 94 \cdot 43(3)^{\circ}$ , Z 2.  $[Ni(bpyam)_2][BF_4]_2.H_2O$ : triclinic, space group  $P\overline{1}$ , a 10.663(5), b 10.861(6), c 12.799(6) Å,  $\alpha$  $68 \cdot 70(4)$ ,  $\beta$  77  $\cdot$  84(4),  $\gamma$  78  $\cdot$  47(4)°, Z 2. [Fe(bpyam)<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub>: orthorhombic, space group P bcn, a  $12 \cdot 317(6), b \ 12 \cdot 609(4), c \ 16 \cdot 644(8) \text{ Å}, Z \ 4.$ 

#### Introduction

The spin state of iron(II) in  $[Fe^{II}N_6]$  systems can be controlled with considerable confidence by the incorporation of appropriate electronic or steric influences into the ligand system. Variation of the donor atom set may also effect a spin state change, but for a particular set, change in spin state is less readily achieved than for  $[Fe^{II}N_6]$  species. Thus the  $[Fe^{II}N_4O_2]$  system, for example, has been found to be almost invariably high spin. A notable recent exception is the complex containing an  $N_4O_2$  sexadentate group derived from 5-nitrosalicylaldehyde and triethylenetetramine.<sup>1</sup> In previous studies of tridentate chelating systems containing an open-chain coordinating substituent in the 2-position of 1,10-phenanthroline it was found that the spin state of iron(II) in the bis(ligand) complexes was strongly dependent on the nature of the donor atom in the substituent. Thus

phenanthroline-2-carbothioamide produces purely singlet state bis(ligand)iron(II) complexes with an  $N_4S_2$ donor atom set, while the corresponding complex of the amide  $(N_4O_2 \text{ donor atom set})$  has a quintet ground state.<sup>2,3</sup> The corresponding complex from 1,10phenanthroline-2-carboxylate, which also contains an  $N_4O_2$  set, similarly is high spin.<sup>4</sup> Coordination of the thioamide sulfur or amide oxygen atom was established from infrared spectral data, though no crystal structure data were obtained. The change in spin state with change in donor atom sequence from  $N_4S_2$ to  $N_4O_2$  can be associated with the relatively high polarizability and nephelauxetic effect of coordinated sulfur, together with its  $\pi$ -acceptor character, all of which will tend to favour spin-pairing in iron(II).<sup>5</sup> In coordinated *bidentate* systems a consistent, though less marked, trend has been observed. Thus the tris(ligand)iron(II) complex of pyridine-2-carboxamide  $(N_3O_3 \text{ set})$  is high spin,<sup>2</sup> while for the corresponding complex of pyridine-2-carbothioamide (N<sub>3</sub>S<sub>3</sub> set) a temperature-induced singlet (<sup>1</sup>A<sub>1</sub>)  $\rightleftharpoons$  quintet (<sup>5</sup>T<sub>2</sub>) transition has been reported.<sup>6</sup>

In the present work the comparison of amide/ thioamide coordination has been extended to the bipyridine-based systems 2,2'-bipyridine-6-carbothioamide (1) (bpytm) and 2,2'-bipyridine-6-carboxamide (2) (bpyam). These represent tridentate extensions of the pyridine systems mentioned above and are obviously closely related to the previously described phenanthroline derivatives. Replacement of the phenanthroline moiety by the bipyridine should result in greater structural flexibility and this may be expected to accommodate the steric constraints of tridentate coordination more readily. The work is thus concerned primarily with a comparison of the field produced by the phenanthroline and bipyridine systems and the structural characterization of the mode of bonding of the substituent groups in six-coordinate iron(II) and nickel(II) complexes.



#### **Results and Discussion**

The ligands (1) and (2) were both obtained from 2,2'-bipyridine-6-carbonitrile, the former by reaction with ammonium sulfide<sup>7</sup> and the latter by copper(II)catalysed hydrolysis.<sup>8</sup> Bis(ligand) complexes of (1) and (2) with iron(II) and nickel(II) were prepared. The electronic properties of the iron(II) complexes of the two ligands are quite different, as was observed for the corresponding phenanthroline systems. Thus salts of  $[Fe(bpytm)_2]^{2+}$  are low spin while those of  $[Fe(byam)_2]^{2+}$  are high spin at room temperature. This difference in spin state is revealed in the room-temperature Mössbauer spectra of [FeL<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub> [L = (1), (2)] shown in Fig. 1. The low values for the isomer shift and quadrupole splitting for the thioamide derivative are indicative of singlet-state iron(II) while the greater values for both parameters for the amide complex are normal for quintet-state iron(II) (Table 1). Comparison with the parameters for the corresponding phenanthroline-based systems reveals very minor differences only (the parameters for the corresponding phenanthroline thioamide complex have been previously reported,<sup>2</sup> while those for the 1,10-phenanthroline-2carboxamide system  $[Fe(phenam)_2][ClO_4]_2$  were measured in the present work (Table 1)).

The low-temperature Mössbauer spectra of  $[Fe(bpyam)_2]$   $[ClO_4]_2.H_2O$  and  $[Fe(bpyam)_2]$ - $[CF_3SO_3]_2.H_2O$ , but not the spectrum of  $[Fe(bpyam)_2]$   $[BF_4]_2$ , reveal a contribution from a small fraction of singlet-state species. Fig. 2 shows the spectra



**Fig. 1.** Mössbauer spectrum at 298 K of: (a) [Fe(bpytm)<sub>2</sub>]-[BF<sub>4</sub>]<sub>2</sub>; (b) [Fe(bpyam)<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub>.

Table 1. Mössbauer	: spectral	l parameters	$(mm s^{-1})$	L)
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Complex	T (K)	$\Delta E_{\rm Q}$	$\delta_{i.s.}$	Spin state
$[Fe(bpytm)_2][BF_4]_2.2H_2O$	298	0.39	$0 \cdot 24$	$^{1}A_{1g}$
	80	0.36	0.31	$^{1}A_{1g}$
$[Fe(bpyam)_2][BF_4]_2$	298	$1 \cdot 80$	0.95	${}^{5}T_{2g}$
	80	$2 \cdot 73$	$1 \cdot 08$	${}^{5}T_{2g}$
[Fe(bpyam) <sub>2</sub> ] [CF <sub>3</sub> SO <sub>3</sub> ] <sub>2</sub> .H <sub>2</sub> O	298	$2 \cdot 04$	0.95	${}^{5}T_{2g}$
	80	$2 \cdot 68$	$1 \cdot 06$	${}^{5}T_{2g}$
	80	0.78	$0 \cdot 43$	$^{1}A_{1g}$
[Fe(bpyam) <sub>2</sub> ] [ClO <sub>4</sub> ] <sub>2</sub> .H <sub>2</sub> O	298	$2 \cdot 26$	0.95	${}^{5}T_{2g}$
	80	$2 \cdot 73$	$1 \cdot 06$	${}^{5}T_{2g}$
	80	0.65	$0 \cdot 46$	$^{1}A_{1g}$
$[Fe(phenam)_2][ClO_4]_2$	298	$2 \cdot 22$	$1 \cdot 04$	${}^{5}\mathrm{T}_{2\mathrm{g}}$

of the perchlorate and triflate salts at 80 K (their room-temperature spectra are very similar to that of the fluoroborate salt shown in Fig. 1). There is thus in these two salts the onset of a quintet  $\rightarrow$  singlet transition at low temperature. There is an obvious influence of the anion on the manifestation of the transition as there is no evidence for this transition in the low-temperature spectrum of the fluoroborate salt. The magnetic data for the complexes are summarized in Table 2 and do not give any distinct indication of the onset of the transition. Mössbauer spectra are, however, more diagnostic of the presence of a low-spin fraction and it should also be noted that the spectra were measured at a temperature lower than the experimental limit available for the measurement of magnetism.

The partial transition to singlet state species observed in salts of  $[Fe(bpyam)_2]^{2+}$  is indicative of a somewhat stronger field than that in the corresponding phenanthroline system. This is confirmed by the ligand field spectrum of  $[Ni(bpyam)_2]^{2+}$ ,  $\nu_1$  (the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$  transition) being observed at a frequency, 11100 cm<sup>-1</sup>, considerably higher than that reported for  $[Ni(phenam)_2]^{2+}$  $(10500 \text{ cm}^{-1})^3$  and certainly consistent with the appearance of singlet-state species in the iron system. The greater field of a bipyridine-derived tridentate compared to that of an analogous phenanthroline-based system has been noted earlier.<sup>9</sup> In the spectra of both  $[Ni(bpytm)_2]^{2+}$  and the previously described<sup>10</sup>  $[Ni(phentm)_2]^{2+} \nu_1$  is observed at 12300 cm<sup>-1</sup>, somewhat lower than in the bis(terpyridine)nickel(II) ion  $(12600 \text{ cm}^{-1})$ ,<sup>11</sup> but sufficiently high to account for the absence of quintet-state species in  $[Fe(bpytm)_2]^{2+}$ or  $[Fe(phentm)_2]^{2+}$ .



Fig. 2. Mössbauer spectrum at 80 K of: (a) [Fe(bpyam)<sub>2</sub>]-[ClO<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O; (b) [Fe(bpyam)<sub>2</sub>] [CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>.H<sub>2</sub>O.

Table 2. Summary of magnetic data for the complexes	Table 2.	Summary	of magnetic	data for	• the	complexes
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-		-	
T (K)	$\mu_{\rm eff}$ (BM)	T(K)	$ \begin{array}{c} \mu_{\rm eff} \\ ({\rm BM}) \end{array} $
353	0.95	303	$0 \cdot 90$
383	0.90	303	0.76
303	$5 \cdot 04$	89	$5 \cdot 01$
303	$5 \cdot 00$	89	$5 \cdot 03$
303	$4 \cdot 95$	89	$4 \cdot 74$
299	1.5		
299	$4 \cdot 89$	184	$4 \cdot 68$
303	$2 \cdot 95$	94	$2 \cdot 89$
303	$2 \cdot 97$	94	$3 \cdot 00$
	$\begin{array}{c} T \\ (K) \\ 353 \\ 383 \\ 303 \\ 303 \\ 303 \\ 299 \\ 299 \\ 299 \\ 303 \\ 303 \\ 303 \end{array}$	$\begin{array}{ccc} T & \mu_{\rm eff} \\ ({\rm K}) & ({\rm BM}) \\ \hline \\ 353 & 0.95 \\ 383 & 0.90 \\ 303 & 5.04 \\ 303 & 5.00 \\ 303 & 4.95 \\ 299 & 1.5 \\ 299 & 1.5 \\ 299 & 4.89 \\ 303 & 2.95 \\ 303 & 2.97 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

<sup>A</sup> In solution.

The electronic spectrum of  $[Fe(bpytm)_2]^{2+}$  shows intense charge-transfer absorption that is split into two components at 15600 and 16950 cm<sup>-1</sup> ( $\epsilon$  6230 and  $6450 \text{ l. mol}^{-1} \text{ cm}^{-1}$ , respectively), with the positions and intensities being indicative of singlet-state  $Fe^{II}$ . This absorption obscures the singlet  $\rightarrow$  singlet ligand field bands. A single, broad charge-transfer band of relatively low intensity, centred at  $19840 \text{ cm}^{-1}$  $(\epsilon \ 1260 \ l. \ mol^{-1} \ cm^{-1})$ , is seen in the spectrum of  $[Fe(bpyam)_2]^{2+}$ . The marked difference in the intensity of the charge transfer in the two systems is a consequence of the difference in spin states which persists in solution, as indicated also by the magnetic data in Table 2. It is noted that within the accessible temperature range there is a small decrease in the magnetic moment for a solution of  $[Fe(bpyam)_2][BF_4]_2$ ; this may indicate the onset of a transition to singlet-state species, as occurs in certain of the solid complexes at lower temperatures. This is supported by the visual thermochromism of the solution—at very low temperatures the colour becomes more intense and the initially red solution becomes red-violet. The *ligand field* spectrum of  $[Fe(bpyam)_2]^{2+}$ at 298 K ( $10^{-2}$  M CH<sub>3</sub>CN solution) shows two well resolved peaks of low intensity at 8850 and 12300  $\rm cm^{-1}$ ( $\epsilon$  18 and 22 l. mol<sup>-1</sup> cm<sup>-1</sup>, respectively). These are characteristic of quintet-state  $Fe^{II}$  and their origin presumably lies in the  ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$  transition, the splitting being associated with low symmetry and/or Jahn Teller effects. They are at somewhat higher frequencies than those reported<sup>3</sup> for  $[Fe(phenam)_2]^{2+}$ , again indicative of the weaker field in this complex.

As for the corresponding phenanthroline-based systems, the different spin states of  $[Fe(bpytm)_2]^{2+}$  and  $[Fe(bpyam)_2]^{2+}$  suggest different donor atom sequences and thus the thioamide and amide groups are expected to coordinate through the sulfur and oxygen atoms, respectively. This is normal for such groups and is supported by infrared spectral data. In the spectrum of the free thioamide a strong absorption at  $1430 \text{ cm}^{-1}$ is assigned to the C–N stretch, while an absorption at  $835 \text{ cm}^{-1}$  is thought to arise from a composite vibration with a contribution from the C=S stretch.<sup>12</sup> In the spectra of  $[Fe(bpytm)_2]$   $[BF_4]_2$  and  $[Ni(bpytm)_2]$   $[BF_4]_2$ the former band moves to higher frequencies (1456 and  $1458 \text{ cm}^{-1}$ , respectively) while the latter moves to lower (810 and  $808 \text{ cm}^{-1}$ , respectively), as observed for the corresponding phenanthroline-based system<sup>2</sup> and consistent with S bonding. For the amide system infrared spectral data are not so diagnostic. The frequency of the C=O stretch is virtually constant at  $1670 \text{ cm}^{-1}$  in the free ligand and in the complexes, while the shifts in the C–N stretch are in accord with oxygen coordination  $(1393 \text{ cm}^{-1} \text{ in the free ligand})$ and  $1408-1410 \text{ cm}^{-1}$  in the complexes). Hydrogen bonding involving the oxygen atom in the free ligand, revealed in the structural studies discussed below, could account for the lack of sensitivity of the C–O stretch to coordination of the group.

#### Structural Studies

The structures of both free ligands (1) and (2) and of the complexes  $[Ni(bpytm)_2] Cl_2.4H_2O$ ,  $[Ni(bpyam)_2] [BF_4]_2.H_2O$  and  $[Fe(bpyam)_2] [BF_4]_2$  have been determined. Suitable crystals of a salt of  $[Fe(bpytm)_2]^{2+}$  could not be grown.

#### Uncoordinated Ligands

A representation of the structure of (1) and the atom numbering scheme are shown in Fig. 3. The numbering scheme for the amide (2) is the same as that for (1), except that S is replaced by O. Bond distances and angles for both structures are listed in Tables 3 and 4, respectively. In both the thioamide (1) and the amide (2), the two pyridine rings adopt a *trans* configuration and, in both structures, the molecules are approximately planar. Previous studies have shown that the uncoordinated bipyridyl moiety can exist in either the *cis* or *trans* configuration or in some non-planar intermediate, by virtue of



Fig. 3. Structure of bpytm (1).

Table 3. Bond lengths (Å) in (1) and (2)In Tables 3–8 and 10–14 estimated standard deviations are<br/>given in parentheses

	0 1		
Atoms	Distance	Distan	ce in $(2)$
	in $(1)$	Molecule $\mathbf{A}$	Molecule B
S-C(11)	$1 \cdot 666(3)$		
O - C(11)		$1 \cdot 234(2)$	$1 \cdot 236(2)$
N(1) - C(1)	$1 \cdot 345(4)$	$1 \cdot 341(2)$	$1 \cdot 330(4)$
N(1)-C(5)	$1 \cdot 336(3)$	$1 \cdot 341(2)$	$1 \cdot 341(3)$
N(2)-C(6)	$1 \cdot 343(3)$	$1 \cdot 344(2)$	$1 \cdot 338(3)$
N(2)-C(10)	$1 \cdot 344(3)$	$1 \cdot 344(2)$	$1 \cdot 337(2)$
N(3)-C(11)	$1 \cdot 312(3)$	$1 \cdot 325(2)$	$1 \cdot 322(2)$
C(1) - C(2)	$1 \cdot 368(5)$	$1 \cdot 369(3)$	$1 \cdot 372(4)$
C(2) - C(3)	$1 \cdot 379(4)$	$1 \cdot 377(3)$	$1 \cdot 371(4)$
C(3) - C(4)	$1 \cdot 379(4)$	$1 \cdot 378(3)$	$1 \cdot 381(3)$
C(4) - C(5)	$1 \cdot 385(4)$	$1 \cdot 385(3)$	$1 \cdot 376(3)$
C(5) - C(6)	$1 \cdot 490(4)$	$1 \cdot 489(2)$	$1 \cdot 489(3)$
C(6) - C(7)	$1 \cdot 383(4)$	$1 \cdot 389(3)$	$1 \cdot 393(3)$
C(7)-C(8)	$1 \cdot 380(4)$	$1 \cdot 381(3)$	$1 \cdot 376(4)$
C(8) - C(9)	$1 \cdot 377(4)$	$1 \cdot 376(3)$	$1 \cdot 377(4)$
C(9)-C(10)	$1 \cdot 379(4)$	$1 \cdot 381(3)$	$1 \cdot 375(3)$
C(10)-C(11)	$1 \cdot 508(4)$	$1 \cdot 505(3)$	$1 \cdot 495(3)$

rotation about the C–C inter-ring bond. The crystal structure of 2,2'-bipyridine alone contains molecules in the planar *trans* configuration;<sup>13,14</sup> however, when crystallized in the presence of I<sub>2</sub>, the molecule (still in an approximately *trans* configuration) becomes twisted, with the angle between the normals to the planes of the aromatic rings being  $49^{\circ}$ .<sup>15</sup> In the presence of KAu(CN)<sub>2</sub>, 2,2'-bipyridine adopts an approximately *cis* configuration with the angle between the normals to the normals to the aromatic ring planes being  $25^{\circ}$ .<sup>16</sup>

The bridging C(5)-C(6) distances in (1) and (2) and in free bipyridine<sup>14</sup> are virtually identical. The dimensions of both the thioamide and amide groups are consistent with those reported for the corresponding pyridine-2carbothioamide<sup>17</sup> and pyridine-2-carboxamide.<sup>18</sup>

Table 4.	Bond	angles	(degrees)	in	(1)	and	(2	)
			( 0 )		``		<b>١</b>	,

Atoms	Angle	Angle	in (2)
	in $(1)$	Molecule $\mathbf{A}$	Molecule B
C(1)-N(1)-C(5)	$116 \cdot 8(3)$	$117 \cdot 4(2)$	$116 \cdot 5(2)$
C(6)-N(2)-C(10)	$117 \cdot 7(2)$	$117 \cdot 4(2)$	$117 \cdot 9(2)$
N(1)-C(1)-C(2)	$124 \cdot 4(3)$	$124 \cdot 1(2)$	$124 \cdot 9(3)$
C(1)-C(2)-C(3)	$117 \cdot 9(3)$	$118 \cdot 1(2)$	$118 \cdot 3(3)$
C(2)-C(3)-C(4)	$119 \cdot 1(3)$	$119 \cdot 0(2)$	$118 \cdot 1(3)$
C(3) - C(4) - C(5)	$119 \cdot 0(3)$	$119 \cdot 4(2)$	$119 \cdot 9(2)$
N(1)-C(5)-C(4)	$122 \cdot 6(3)$	$121 \cdot 9(2)$	$122 \cdot 4(2)$
N(1)-C(5)-C(6)	$116 \cdot 2(2)$	$117 \cdot 0(2)$	$115 \cdot 9(2)$
C(4) - C(5) - C(6)	$121 \cdot 1(2)$	$121 \cdot 2(2)$	$121 \cdot 7(2)$
N(2)-C(6)-C(5)	$115 \cdot 8(2)$	$116 \cdot 7(2)$	$116 \cdot 2(2)$
N(2) - C(6) - C(7)	$122 \cdot 3(2)$	$122 \cdot 2(2)$	$121 \cdot 9(2)$
C(5)-C(6)-C(7)	$121 \cdot 9(2)$	$121 \cdot 1(2)$	$121 \cdot 9(2)$
C(6) - C(7) - C(8)	$119 \cdot 0(2)$	$119 \cdot 1(2)$	$119 \cdot 0(2)$
C(7)-C(8)-C(9)	$119 \cdot 3(3)$	$119 \cdot 5(2)$	$119 \cdot 4(2)$
C(8) - C(9) - C(10)	$118 \cdot 3(2)$	$118 \cdot 0(2)$	$118 \cdot 1(2)$
N(2)-C(10)-C(9)	$123 \cdot 3(2)$	$123 \cdot 9(2)$	$123 \cdot 7(2)$
N(2)-C(10)-C(11)	$114 \cdot 0(2)$	$117 \cdot 0(2)$	$117 \cdot 0(2)$
C(9)-C(10)-C(11)	$122 \cdot 7(2)$	$119 \cdot 1(2)$	$119 \cdot 3(2)$
N(3)-C(11)-C(10)	$114 \cdot 4(2)$	$116 \cdot 4(2)$	$117 \cdot 3(2)$
S-C(11)-N(3)	$123 \cdot 8(2)$		
S-C(11)-C(10)	$121 \cdot 7(2)$		
O-C(11)-N(3)	. /	$123 \cdot 6(2)$	$122 \cdot 7(2)$
O-C(11)-C(10)		$119 \cdot 9(2)$	$120 \cdot 0(2)$



**Fig. 4.** The hydrogen bonding in (2) showing a chain of dimers (along b) of **B** molecules bridged by pairs of **A** molecules. The additional hydrogen bonding from the amide of molecules **A** to the pyridine of molecules **A** is not shown.

As was expected from infrared spectral data in particular, in the free amide (2) there is an extensive network of hydrogen bonding within the structure. The nature of the hydrogen bonding is represented in Fig. 4. Pairs of molecules **B** form dimers through two  $O \cdots NH_2$  linkages, the  $NH \cdots O$  distance being  $2 \cdot 02$  Å. There is a centre of inversion that relates the two molecules involved. Molecule **A** is approximately orthogonal to molecule **B**; however, it is involved in a hydrogen-bonding pattern that is different to that for molecule **B**. Dimers of molecule **B** are linked in chains by pairs of amide groups of molecules of **A** through hydrogen bonding of the type:

$N - H \cdots O = C - N - H \cdots O$					
В	Α	В			
dimer 1	amide	dimer 2			

Molecule **A** is also involved in a second type of hydrogen-bonding interaction. This involves the amide group hydrogen atom, which is not involved in linking **B** dimers, hydrogen-bonding to the N(1) atom of the pyridine ring of a symmetry-related **A** molecule. The hydrogen bonding results in layers in the yz-plane from which **B** molecules protrude on both sides. Layers pack by interspersing protruding **B** molecules. There are both edge-to-face and face-to-face aromatic interactions between molecules. The pyridine rings of molecule **B** are not involved in any hydrogen bonding.

Hydrogen bonding in (1) is restricted to that which occurs between pairs of molecules through  $S \cdots NH_2$ linkages, the N–H $\cdot\cdot\cdot$ S hydrogen bond distances being  $2 \cdot 48$  Å. This results in the formation of centrosymmetric planar dimeric units analogous to those described above for (1). There is face-to-face aromatic stacking of the dimeric units. The pyridine  $\operatorname{ring} \cdots$  pyridine ring distances of the adjacent 'stacked' molecules are approximately  $3 \cdot 4$  Å. The question arises as to why these two very similar molecules pack so differently in the solid state. The differences between the two molecules are the C=S distance, which is some 0.4 Å longer than the C=O distance, and the difference in the propensity for hydrogen bonding to O as against S. It is likely that the first of these differences could easily be accommodated if (2) adopted the packing of (1) by a small change in unit cell dimensions. It seems, therefore, that it is the more extensive hydrogen bonding which dictates the molecular packing of (2)and the concomitant incorporation of a second molecule into the asymmetric unit. It is noteworthy that in the corresponding pyridine systems the packing and the hydrogen-bonding pattern is essentially the same for the amide and thioamide<sup>17,18</sup> and includes the formation of dimers analogous to those observed in the present work.

#### Metal Complexes

Fig. 5 shows the structure of the complex cation in  $[Ni(bpytm)_2]$  Cl<sub>2</sub>.4H<sub>2</sub>O and the atom numbering

scheme. Bond lengths and selected bond angles are listed in Tables 5 and 6. The two bpytm molecules are tridentate and their coordination planes are nearly orthogonal with the angle between the normals to the two planes being  $88 \cdot 8^{\circ}$ . Coordination occurs through the two nitrogen atoms of the pyridine rings and the sulfur atom of the thioamide group, as was expected. The environment about the Ni atom is considerably distorted from regular octahedral, as evidenced, for example, by the disparity in the metal-to-donor atom distances. Average values for Ni–N<sub>distal</sub>, Ni–N<sub>central</sub> and Ni–S are  $2 \cdot 090(3), 2 \cdot 034(3)$  and  $2 \cdot 419(1)$  Å, severally. The Ni–S distances are consistent with those reported for other systems.<sup>19</sup> The Ni–N<sub>distal</sub> and Ni–N<sub>central</sub> distances are similar to those for  $[Ni(terpy)_2]^{2+}$ ,<sup>20</sup> and for the struct-urally related complex  $[Ni(bph)_2]^{2+}$ , where bph is 2,2'bipyridine-6-carbaldehyde phenylhydrazone,<sup>10</sup> though the Ni– $N_{central}$  distance in  $[Ni(bpytm)_2]Cl_2.4H_2O$  is somewhat longer than in these two related complexes. This relatively long distance in the thioamide complex may be imposed by the large sulfur atom in an adjacent chelate ring. It is primarily the size of this atom which leads to important differences in the geometry of the two chelate rings associated with each ligand molecule. Thus the greater C(11)-S distance compared with the C(5)-N(1) distance places the S atom in a more favourable coordination site, as reflected in the values for the S–Ni–N(2) (81  $\cdot$  8°) and N(1)–Ni–N(2)  $(78 \cdot 9^{\circ})$  bite angles, the former being closer to the normal octahedral angle. The bite angle N(1)-Ni-N(2)is similar to the average value of the bite angle in  $[Ni(terpy)_2]^{2+}$  (77.9°) and also the analogous angle in  $[Ni(bph)_2]^{2+}$  (78.3°).

The crystal structure consists of discrete layers perpendicular to b (Fig. 6). Cation layers are separated by layers of water molecules and chloride ions which are extensively hydrogen-bonded. The amine hydrogen atoms also take part in the hydrogen bonding and form the only interactions between the cation and anion (chloride) layers. Each amine nitrogen atom hydrogen-bonds to one water molecule and one chlorine atom, and hence is a donor to two hydrogen bonds. The water molecules form an additional hydrogen-bonded network and are also found to hydrogen-bond to the chlorine atoms. There are two types of chlorine atoms with respect to the nature of hydrogen bonding. One is an acceptor for four hydrogen bonds, the  $Cl \cdots H$ distances being  $2 \cdot 18$ ,  $2 \cdot 23$ ,  $2 \cdot 29$  and  $2 \cdot 33$  Å. The second type is an acceptor for two hydrogen bonds with  $Cl \cdot \cdot \cdot H$  bond distances of  $2 \cdot 22$  and  $2 \cdot 28$  Å. In each of these cases the longest hydrogen bond is associated with an amide hydrogen atom. These distances are within the normal ranges observed for such interactions, and correspond closely to those in, for example, bis[2,2'-iminobis(acetamidoxime)]nickel(II) chloride dihydrate.<sup>21</sup>

Fig. 7 shows the structure of the complex cation in  $[Fe(bpyam)_2][BF_4]_2$  and the atom numbering scheme.

Fig. 5. Structure this diagram ligar

N(3

Table 5.	Bond o	distances	(Å) for	r
[Ni(	bpytm)	2] Cl <sub>2</sub> .4H	<sub>2</sub> 0	

-		
Atoms	Ligand $A$	Ligand $B$
Ni-S	$2 \cdot 441(1)$	$2 \cdot 397(1)$
Ni-N(1)	$2 \cdot 095(3)$	$2 \cdot 084(3)$
Ni-N(2)	$2 \cdot 031(3)$	$2 \cdot 036(3)$
S-C(11)	1.685(4)	$1 \cdot 674(4)$
N(1) - C(1)	$1 \cdot 341(5)$	$1 \cdot 340(5)$
N(1) - C(5)	$1 \cdot 354(5)$	$1 \cdot 352(4)$
N(2) - C(6)	$1 \cdot 338(5)$	$1 \cdot 351(5)$
N(2) - C(10)	$1 \cdot 346(4)$	$1 \cdot 345(5)$
N(3) - C(11)	$1 \cdot 324(5)$	$1 \cdot 305(5)$
C(1) - C(2)	$1 \cdot 377(6)$	$1 \cdot 386(6)$
C(2) - C(3)	$1 \cdot 367(6)$	$1 \cdot 365(6)$
C(3) - C(4)	$1 \cdot 378(6)$	$1 \cdot 383(6)$
C(4) - C(5)	$1 \cdot 373(5)$	$1 \cdot 389(5)$
C(5) - C(6)	$1 \cdot 476(5)$	$1 \cdot 472(5)$
C(6) - C(7)	$1 \cdot 392(5)$	$1 \cdot 391(5)$
C(7)-C(8)	$1 \cdot 384(6)$	$1 \cdot 357(6)$
C(8) - C(9)	$1 \cdot 369(6)$	$1 \cdot 393(6)$
C(9) - C(10)	$1 \cdot 382(5)$	1.378(5)
C(10)-C(11)	$1 \cdot 483(5)$	$1 \cdot 496(5)$

SA-Ni-N(1)A		$160 \cdot 0(1)$	
SA-Ni-N(2)A		$81 \cdot 8(1)$	
SA-Ni-N(1)B		89.7(1)	
SA-Ni-N(2)B		$103 \cdot 9(1)$	
N(1)A-Ni-N(2)A		$78 \cdot 9(1)$	
N(1)A-Ni-N(1)B		$91 \cdot 0(1)$	
N(1)A-Ni-N(2)B		$95 \cdot 8(1)$	
SA–Ni–SB		$92 \cdot 6(0)$	
SB-Ni-N(1)B		$161 \cdot 1(1)$	
SB-Ni-N(2)B		$82 \cdot 5(1)$	
N(1)A-Ni-SB		$93 \cdot 2(1)$	
N(2)A-Ni-SB		$92 \cdot 0(1)$	
N(1)B-Ni-N(2)B		$78 \cdot 8(1)$	
N(2)A-Ni-N(2)B		$172 \cdot 2(1)$	
N(2)A-Ni-N(1)B		$106 \cdot 8(1)$	
	Ligand A		Ligand B
$N_{i}=S=C(11)$	07.2(1)		08.4(1)
Ni-N(1)-C(1)	127.5(3)		126.3(3)
Ni - N(1) - C(5)	$121 \cdot 0(0)$ $114 \cdot 2(2)$		$120 \cdot 5(3)$ 114.5(2)
C(1) - N(1) - C(5)	$114 \cdot 2(2)$ $118 \cdot 3(3)$		114.3(2) 110.3(3)
$N_{i}-N(2)-C(6)$	116.1(2)		116.3(3)
Ni - N(2) - C(10)	$110^{1}1(2)$ 123.2(2)		123.1(2)
C(6) - N(2) - C(10)	$129 \cdot 2(2)$ $119 \cdot 6(3)$		$120 \cdot 1(2)$ $120 \cdot 3(3)$
N(1)-C(1)-C(2)	122.5(4)		$120 \ 0(0)$ 121.9(4)
C(1) - C(2) - C(3)	118.6(4)		$121 \ 3(4)$ 118.7(4)
C(2)-C(3)-C(4)	110.0(1)		120.3(4)
C(3)-C(4)-C(5)	118.9(4)		118.4(4)
N(1)-C(5)-C(4)	$121 \cdot 8(4)$		$121 \cdot 4(4)$
N(1) - C(5) - C(6)	114.5(3)		$115 \cdot 3(3)$
C(4)-C(5)-C(6)	$123 \cdot 7(4)$		$123 \cdot 4(4)$
N(2)-C(6)-C(5)	115.6(3)		$114 \cdot 8(3)$
N(2)-C(6)-C(7)	$121 \cdot 6(4)$		120.6(4)
C(5)-C(6)-C(7)	$122 \cdot 7(4)$		$124 \cdot 6(3)$
C(6)-C(7)-C(8)	$118 \cdot 1(4)$		$119 \cdot 2(4)$
C(7)-C(8)-C(9)	$120 \cdot 2(4)$		$120 \cdot 3(4)$
C(8)-C(9)-C(10)	$118 \cdot 9(4)$		118.6(4)
N(2) - C(10) - C(9)	$121 \cdot 5(3)$		$121 \cdot 0(3)$
N(2) - C(10) - C(11)	$115 \cdot 2(3)$		$115 \cdot 3(3)$
C(9) - C(10) - C(11)	$123 \cdot 3(3)$		$123 \cdot 6(4)$
S-C(11)-N(3)	$121 \cdot 1(3)$		$121 \cdot 4(3)$
S-C(11)-C(10)	$121 \cdot 1(3)$		120.7(3)
N(3) - C(11) - C(10)	$117 \cdot 8(3)$		$117 \cdot 9(3)$
	. /		( )



 $\label{eq:Fig. 6.} \mbox{ Hydrogen bonding in } [Ni(bpytm)_2] \, Cl_2.4 H_2 O.$ In the hydrogen-bonded layers the oxygen atoms are represented as filled circles while the chlorine atoms are diagonally hatched.

s <sup>r</sup>	Atoms	Angle	
C(11)	SA-Ni-N(1)A	$160 \cdot 0(1)$	
	SA-Ni-N(2)A	$81 \cdot 8(1)$	
	SA-Ni-N(1)B	89.7(1)	
	SA-Ni-N(2)B	$103 \cdot 9(1)$	
$\sim \frac{1}{N(1)}$	N(1)A-Ni-N(2)A	$78 \cdot 9(1)$	
N(2) Ni QN(2)	N(1)A-Ni-N(1)B	$91 \cdot 0(1)$	
s S	N(1)A-Ni-N(2)B	$95 \cdot 8(1)$	
CIER	SA–Ni–SB	$92 \cdot 6(0)$	
C(0)	SB-Ni-N(1)B	$161 \cdot 1(1)$	
N(I)	SB-Ni-N(2)B	$82 \cdot 5(1)$	
C(5)	N(1)A-Ni-SB	$93 \cdot 2(1)$	
$C(1)^{(1)}$	N(2)A-Ni-SB	$92 \cdot 0(1)$	
C(4)	N(1)B-Ni-N(2)B	$78 \cdot 8(1)$	
	N(2)A-Ni-N(2)B	$172 \cdot 2(1)$	
C(2) C(3)	N(2)A-Ni-N(1)B	$106 \cdot 8(1)$	
		Ligand $A$	Ligand A
U	Ni-S-C(11)	$97 \cdot 2(1)$	$98 \cdot 4(1)$
the complex cation $[Ni(bpytm)_2]^{2+}$ . In	Ni-N(1)-C(1)	$127 \cdot 5(3)$	$126 \cdot 3(3)$
1 is vertical.	Ni-N(1)-C(5)	$114 \cdot 2(2)$	114.5(2)
	C(1) - N(1) - C(5)	118.3(3)	119.3(3)
	Ni-N(2)-C(6)	$116 \cdot 1(2)$	116.3(3)

The structure of the cation in  $[Ni(bpyam)_2]$  [BF<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O is essentially the same and the same numbering scheme applies, though for this complex there are two independent ligand molecules, A and B. Bond distances and selected bond angles for both complexes are listed in Tables 7 and 8, respectively. The coordination about each metal atom is distorted octahedral with the two bpyam molecules coordinating meridionally through the two pyridine nitrogens and the amide oxygen atoms.

In the iron complex the two ligands are related by a twofold axis of symmetry that runs through the iron atom. The angle between the normals to the two ligand planes is  $76 \cdot 9^{\circ}$ . Iron-donor atom distances are normal for high-spin iron(II). Distortion of the coordination sphere shows up markedly in the angles about the metal atom; bite angles of  $74 \cdot 1$  and  $73 \cdot 7^{\circ}$  were found for the NN and NO chelate rings, respectively. The overall bite angle ( $147 \cdot 6^{\circ}$ ) is comparable to that in the *high-spin* complex of the NNN donor 2,6-bis(triazol-



**Fig. 7.** Structure of the complex cation in  $[Fe(bpyam)_2]$   $[BF_4]_2$ . The structure of the cation in  $[Ni(bpyam)_2]$   $[BF_4]_2$ .H<sub>2</sub>O is essentially the same but with two independent ligands, A and B.

Table 7. Bond lengths (A) in	
$[M(bpyam)_2] [BF_4]_2 (M = Ni, Fe)$	
Symmetry transformation: $^{i}1-x, y, \frac{1}{2}$	-z

*.* • .

Atoms	M =	= Ni	$\mathbf{M}=\mathbf{F}\mathbf{e}$
	Ligand $A$	Ligand $B$	
M–O	$2 \cdot 136(5)$	$2 \cdot 110(5)$	$2 \cdot 174(5)$
M-N(1)	$2 \cdot 095(6)$	$2 \cdot 084(6)$	$2 \cdot 180(6)$
M-N(2)	1.982(6)	1.988(5)	$2 \cdot 096(5)$
O - C(11)	$1 \cdot 245(9)$	$1 \cdot 248(8)$	$1 \cdot 247(9)$
N(1) - C(1)	$1 \cdot 324(10)$	$1 \cdot 321(9)$	$1 \cdot 334(9)$
N(1)-C(5)	$1 \cdot 341(9)$	$1 \cdot 346(9)$	$1 \cdot 336(8)$
N(2)-C(6)	$1 \cdot 344(9)$	$1 \cdot 338(9)$	$1 \cdot 335(9)$
N(2)-C(10)	$1 \cdot 323(9)$	$1 \cdot 321(9)$	$1 \cdot 342(9)$
N(3)-C(11)	$1 \cdot 325(10)$	$1 \cdot 302(9)$	$1 \cdot 316(9)$
C(1)-C(2)	$1 \cdot 381(11)$	$1 \cdot 369(12)$	$1 \cdot 414(11)$
C(2)-C(3)	$1 \cdot 385(12)$	$1 \cdot 351(13)$	$1 \cdot 348(12)$
C(3)-C(4)	$1 \cdot 369(13)$	$1 \cdot 395(13)$	$1 \cdot 387(11)$
C(4) - C(5)	$1 \cdot 393(10)$	$1 \cdot 388(11)$	$1 \cdot 384(10)$
C(5)-C(6)	$1 \cdot 464(11)$	$1 \cdot 479(10)$	$1 \cdot 484(10)$
C(6)-C(7)	$1 \cdot 394(10)$	$1 \cdot 402(10)$	$1 \cdot 384(10)$
$\rm C(7)–C(8)$	$1 \cdot 369(13)$	$1 \cdot 370(12)$	$1 \cdot 384(11)$
C(8)-C(9)	$1 \cdot 398(12)$	$1 \cdot 378(12)$	$1 \cdot 405(11)$
C(9)-C(10)	$1 \cdot 371(10)$	$1 \cdot 377(10)$	$1 \cdot 362(10)$
C(10)-C(11)	$1 \cdot 520(11)$	$1 \cdot 515(10)$	$1 \cdot 503(10)$

3-yl)pyridine<sup>22</sup> but considerably less than that in the low-spin terpy complex  $(161 \cdot 0(3)^{\circ})$ ,<sup>23</sup> and the difference arises from the different radii of high-spin and low-spin iron(II). The structure of the low-spin [Fe<sup>II</sup>N<sub>6</sub>] derivative of the tridentate N-pyridin-2-ylcarbonyl-pyridine-2-carboximinate ion<sup>24</sup> is of relevance here since it also involves the coordination of two pyridine nitrogens and an amide group. The ligand system differs importantly from bypam, however, in that the amide group is flanked by the two pyridine rings and thus it coordinates through the nitrogen atom, oxygen coordination being sterically unfavourable for tridentate function in this instance. A further significant difference is that the amide group is deprotonated, again favouring nitrogen coordination in this instance.

Table 8. Bond angles (degrees) in  $[M(bpyam)_2][BF_4]_2$  (M = Ni, Fe)

Atoms		$\mathbf{M}=\mathbf{N}\mathbf{i}$		$\mathbf{M}=\mathbf{F}\mathbf{e}$
OA–Ni–OB		$87 \cdot 9(2)$		
N(1)A-Ni- $N(1)B$		$92 \cdot 8(2)$		
N(2)A-Ni-N(2)B		$176 \cdot 4(2)$		
OA-Ni-N(1)B		$94 \cdot 5(2)$		
OA-Ni-N(2)B		$99 \cdot 9(2)$		
N(1)A-Ni-OB		$94 \cdot 3(2)$		
N(2)A-Ni-OB		$100 \cdot 0(2)$		
N(1)A-Ni- $N(2)B$		$103 \cdot 9(2)$		
N(2)A-Ni-N(1)B		$103 \cdot 5(2)$		
O–Fe–O <sup>i</sup>				$90 \cdot 3(3)$
$N(1)$ –Fe– $N(1)^{i}$				87.0(3)
$N(2)$ -Fe- $N(2)^{i}$				$176 \cdot 2(3)$
$O-Fe-N(1)^{i}$				$100 \cdot 3(2)$
$O-Fe-N(2)^{i}$				$103 \cdot 5(2)$
$N(1)$ –Fe– $N(2)^{i}$				$108 \cdot 8(2)$
	Ligand $A$		Ligand $B$	
O-M-N(1)	156.0(2)		156.4(2)	147.6(2)
O-M-N(2)	77.5(2)		77.3(2)	73.7(2)
N(1)-M-N(2)	78.6(2)		79.1(2)	$74 \cdot 1(2)$
$M_{-}O_{-}C(11)$	113.5(5)		114.8(5)	117.3(5)
M = N(1) = C(1)	$127 \cdot 1(5)$		$128 \cdot 1(5)$	$123 \cdot 6(5)$
M-N(1)-C(5)	113.5(5)		113.6(5)	$117 \cdot 2(5)$
C(1)-N(1)-C(5)	$119 \cdot 3(7)$		$118 \cdot 3(6)$	$118 \cdot 5(7)$
M-N(2)-C(6)	118.6(5)		$118 \cdot 2(5)$	120.0(5)
M-N(2)-C(10)	$119 \cdot 9(5)$		119.5(5)	$120 \cdot 2(5)$
C(6)-N(2)-C(10)	$121 \cdot 4(6)$		$122 \cdot 3(6)$	119.5(6)
N(1)-C(1)-C(2)	$122 \cdot 8(8)$		$123 \cdot 2(8)$	$121 \cdot 5(8)$
C(1)-C(2)-C(3)	117.6(8)		$118 \cdot 8(9)$	119.1(8)
C(2)-C(3)-C(4)	120.6(8)		120.3(8)	119.7(8)
C(3)-C(4)-C(5)	118.0(8)		$117 \cdot 1(8)$	$118 \cdot 3(7)$
N(1)-C(5)-C(4)	$121 \cdot 7(8)$		$122 \cdot 3(8)$	$122 \cdot 8(7)$
N(1)-C(5)-C(6)	$115 \cdot 8(6)$		$115 \cdot 4(6)$	113.7(6)
C(4)-C(5)-C(6)	$122 \cdot 5(7)$		$122 \cdot 3(7)$	$123 \cdot 5(7)$
N(2)-C(6)-C(5)	$113 \cdot 4(6)$		$113 \cdot 6(6)$	$114 \cdot 1(6)$
N(2)-C(6)-C(7)	$119 \cdot 4(8)$		$119 \cdot 3(7)$	$120 \cdot 8(7)$
C(5)-C(6)-C(7)	$127 \cdot 2(7)$		$127 \cdot 1(7)$	$125 \cdot 1(7)$
C(6)-C(7)-C(8)	$119 \cdot 2(8)$		$118 \cdot 3(8)$	119.5(8)
C(7)-C(8)-C(9)	120.5(7)		$121 \cdot 1(7)$	119.4(7)
C(8)-C(9)-C(10)	$117 \cdot 2(8)$		$117 \cdot 9(8)$	$117 \cdot 1(7)$
N(2)-C(10)-C(9)	$122 \cdot 4(7)$		$121 \cdot 1(7)$	$123 \cdot 7(7)$
N(2)-C(10)-C(11)	110.8(6)		$111 \cdot 2(6)$	110.7(6)
C(9)-C(10)-C(11)	$126 \cdot 9(8)$		$127 \cdot 7(7)$	$125 \cdot 6(7)$
O-C(11)-N(3)	$123 \cdot 0(7)$		$123 \cdot 2(7)$	$123 \cdot 2(7)$
O-C(11)-C(10)	$118 \cdot 1(7)$		116.9(6)	117.7(7)
N(3) - C(11) - C(10)	$118 \cdot 8(7)$		$119 \cdot 9(7)$	$119 \cdot 1(7)$
	( )		()	(*)

The environment aboutthe Ni  $\operatorname{atom}$ in  $[Ni(bpyam)_2]^{2+}$  shows considerable distortion from octahedral symmetry. The average Ni–N<sub>distal</sub> distance is  $2 \cdot 090$  Å while the average Ni–N<sub>central</sub> distance is 1.985 Å. These distances are comparable to those reported for  $[Ni(bph)_2]^{2+}$ ,<sup>10</sup> but are slightly *less* than those of  $[Ni(terpy)_2]^{2+}$ .<sup>20</sup> Despite this, the ligand field of bpyam is weaker than that of terpyridine. This highlights the importance of the actual donor-atom set in determining the overall field strength. The average Ni–O distance is  $2 \cdot 123$  Å, somewhat longer than that found in the diaqua-bis(pyridine-2-carboxamide)nickel(II) cation (2.045 Å), where the constraints of tridentate coordination do not apply.<sup>25</sup> The metal-todonor atom distances in the Ni<sup>II</sup> complex of bpyam are significantly shorter than those of the Fe<sup>II</sup> complex. This is also reflected in the greater bite angles of the  $Ni^{II}$  complex (average  $78 \cdot 9^{\circ}$  for the NN chelate loop and  $77 \cdot 4^{\circ}$  for the NO loop) and is expected to be a result of the smaller ionic radius of Ni<sup>II</sup>, compared to that of high-spin iron(II). The average overall bite angle is  $156 \cdot 2^{\circ}$  which is in good agreement with those of the  $[Ni(bph)_2]^{2+}$  and  $[Ni(terpy)_2]^{2+}$  systems.<sup>10,20</sup>

The lattice water in  $[Ni(bpyam)_2][BF_4]_2.H_2O$  is involved in hydrogen bonding within the structure. The cations are linked in pairs by hydrogen-bonding to two water molecules. Such hydrogen bonding occurs through linkages of the type:

#### $NH_{amide} \cdots O - H_{water} \cdots O_{amide}$

The hydrogen bonding involving the NH group appears to be slightly stronger than that involving the O atom of the amide group, the distances being 2.921 and 2.959 Å, respectively. A similar type of hydrogen bonding, which would strengthen the  $\sigma$ -bonding capacity of the amide group, may also occur in the hydrated perchlorate and triflate salts of the bis(ligand)Fe<sup>II</sup> complexes, accounting for the occurrence of a small low-spin fraction in these salts at low temperature, in contrast to the purely high-spin nature of the fluoroborate salt which was obtained anhydrous.

In  $[Fe(bpyam)_2][BF_4]_2$  the only hydrogen bonding involves interactions of the type  $NH \cdot \cdot \cdot F$  which link the complex cation to the counter anion. The same kind of interaction is also present in  $[Ni(bpyam)_2][BF_4]_2.H_2O$ . There are two distinct distances for these interactions in each complex, these being 1.90 and 1.92 Å for the iron(II) complex and 1.96 and 2.00 Å for the nickel(II) complex.

Comparison of the dimensions of the free ligands (1) and (2) with those of the coordinated ligands reveals small changes in the directions which would be expected for coordination. However, the standard deviations for the measured S–C(11), O–C(11) and N(3)–C(11) distances in both the iron and nickel complexes are relatively large and hence the small changes in these distances resulting from coordination might not be

significant. The S–C(11) and N(3)–C(11) distances appear longer and shorter, respectively, in the Ni complex compared to the distances in the free ligand, and this is as expected for sulfur coordination. The only significant geometrical change in the pyridine rings on coordination would seem to be the greater C–N–C angles (i.e. 116.8 and 117.7° for the uncoordinated ligand; cf. average values of 118.8 and 120.0° for the coordinated ligand). The same trends are observed in (2). In all three metal complexes, the ligands are approximately planar.

#### Concluding Comments

Infrared spectral data, in particular those relating to  $\nu_{C=S}$  and  $\nu_{C=O}$ , seem to offer a reliable guide to the coordination mode of the thioamide or amide group in the present systems. However, the shifts observed in frequencies relating to these vibrations in the complexes are not reflected in any major observed changes in the bond distances within the functional groups on coordination. The changes which are observed, though generally in the directions expected, cannot be considered significant in view of the degree of precision of the measured distances.

Comparison of the geometry of the free ligand with that of the coordinated ligand reveals that for the thioamide group there is little change in the C(10)-C(11)-S angle on coordination, whereas the C(10)-C(11)-O angle in the coordinated amide group is significantly smaller than that in the free amide. The sulfur atom is thus better positioned for coordination in the tridentate system. This is also evident from the angles about the metal atom in the chelate rings. Whereas in the nickel thioamide complex the deviation from the ideal angle of 90° is less for the S–Ni–N angle than for the N–Ni–N angle, for both the nickel and iron complexes of the amide the deviation is *greater* for the O-M-N angles than for the N-M-N angles. This more favourable geometry of the coordinated thioamide group may contribute to its observed stronger ligand field and hence the fundamental difference in the ground state for the bis(ligand)iron(II) complexes.

#### Experimental

#### Preparations

2,2'-Bipyridine-6-carbothioamide (1) was prepared from 2,2'bipyridine-6-carbonitrile according to the procedure reported by Antonini *et al.*,<sup>7</sup> m.p. 176–177°C (lit.<sup>7</sup> 177–178°C). The following synthesis of 2,2'-bipyridine-6-carboxamide (2) was based upon the method of Breslow *et al.*<sup>8</sup> for the metal ion catalysed hydrolysis of 1,10-phenanthroline-2-carbonitrile to the corresponding amide. To a solution of 2,2'-bipyridine-6-carbonitrile (1·0 g, 5·5 mmol) in H<sub>2</sub>O (60 ml) was added CuCl<sub>2</sub>.2H<sub>2</sub>O (0·94 g, 5·53 mmol) and the resultant green/blue solution was titrated with NaOH (0·5 M) to pH 11. At this pH a pale blue solid had formed and ethylenediaminetetraacetic acid (4·12 g, 11·1 mmol) in H<sub>2</sub>O (15 ml) was then added, a process resulting in a clear blue solution of pH 5. The solution was adjusted to pH 7 with NaOH (0·5 M) at which point a white precipitate formed. The solid was collected by filtration, washed with cold H<sub>2</sub>O and suction-dried. The solid was recrystallized from ethanol/diethyl ether to yield white *needles* (0.83 g, 75.5%), m.p. 151–153°C (Found: C, 66.4; H, 4.5; N, 21.2. C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O requires C, 66.3; H, 4.5; N, 21.1%).

All iron complexes were prepared under a nitrogen atmosphere. The following procedure was used for the preparation of both iron and nickel complexes. The solid ligand (2 mmol) was added to a warm aqueous (20%) ethanol solution (10 ml) of the metal chloride (1 mmol). The solution was warmed until the ligand had reacted and was then filtered. To the filtrate an excess of an aqueous solution of the appropriate sodium or ammonium salt was added and the complex salt crystallized on cooling. This was washed with cold water and dried in a vacuum desiccator over phosphorus pentoxide. Analytical data for the complexes are listed in Table 9.

Table 9. Analytical data for the complexes

Com-	L Found (%)					Requires (%)			
plex		$\mathbf{C}$	Η	N	Μ	$\mathbf{C}$	Η	N	Μ
$[FeL_2][BF_4]_2.2H_2O$	(1)	$38 \cdot 1$	$3 \cdot 0$	$12 \cdot 0$	$7 \cdot 8$	$38 \cdot 0$	$3 \cdot 2$	$12 \cdot 1$	$8 \cdot 0$
$[NiL_2][BF_4]_2.H_2O$	(1)	$39 \cdot 2$	$3 \cdot 3$	$12 \cdot 2$	$8 \cdot 5$	$38 \cdot 8$	$2 \cdot 9$	$12 \cdot 4$	$8 \cdot 6$
$[FeL_2][BF_4]_2$	(2)	$41 \cdot 9$	$3 \cdot 2$	$13 \cdot 5$	$8 \cdot 9$	$42 \cdot 1$	$2 \cdot 9$	$13 \cdot 4$	$8 \cdot 9$
$[FeL_2]$ $[ClO_4]_2.H_2O$	(2)	$39 \cdot 5$	$3 \cdot 2$	$12 \cdot 6$	$8 \cdot 5$	$39 \cdot 4$	$3 \cdot 0$	$12 \cdot 5$	$8 \cdot 3$
$[FeL_2][CF_3SO_3]_2.H_2O$	(2)	$37 \cdot 4$	$2 \cdot 9$	$10 \cdot 8$	$7 \cdot 4$	$37 \cdot 4$	$2 \cdot 6$	$10 \cdot 9$	$7 \cdot 3$
$[FeL_2]$ I <sub>2</sub> .3H <sub>2</sub> O	(2)	$35 \cdot 2$	$3 \cdot 2$	$10 \cdot 9$	$7 \cdot 2$	$34 \cdot 7$	$3 \cdot 2$	$11 \cdot 0$	$7 \cdot 3$
$[NiL_2] [BF_4]_2.H_2O$	(2)	$41 \cdot 1$	$3 \cdot 4$	$13 \cdot 0$	$8 \cdot 9$	$40 \cdot 7$	$3 \cdot 1$	$13 \cdot 0$	$9\cdot 1$

#### **Physical Measurements**

#### Magnetism

The magnetic data for solid samples were obtained by using a Newport variable temperature Gouy balance calibrated with CoHg(NCS)<sub>4</sub>. Magnetic data for samples in methanol solution were obtained by the Evans<sup>26</sup> method with a BRUKER AM-500 n.m.r. spectrometer. The method was modified according to the description of Baker, Field and Hambley<sup>27</sup> for application with a superconducting magnet. The sample temperature was calibrated by using the known temperature-dependence of the spectrum of methanol as a reference standard. Correction for the temperature-dependence of the density of the solvent<sup>28</sup> has been made. All data have been corrected for diamagnetism calculated by using Pascal's constants.<sup>29</sup>

#### Spectra

Mössbauer spectra were recorded with a constant acceleration spectrometer in transmission mode. The source was <sup>57</sup>Co in a rhodium matrix. The temperature was controlled by an Oxford Instruments CF506 continuous-flow cryostat together with an ITC-4 temperature control unit. The isomer shift values quoted are relative to the midpoint of the iron spectrum at room temperature. The spectral parameters were extracted from a least-squares fit of the data to Lorentzian line shapes. Electronic spectra were recorded for acetonitrile solutions on a Cary 17 spectrophotometer. Infrared spectra were measured on an ATI Mattson Genesis Fourier-transform spectrometer for samples prepared as compressed CsI disks.

#### Crystallography

#### Crystal Data

For bpytm. Crystals were grown from ethanol. C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>S, M 215·3, monoclinic, space group  $P 2_1/c$ , a 8·265(3), b 11·175(2), c 11·114(4) Å,  $\beta$  94·47(2)°, V 1023·4(5) Å<sup>3</sup>, D<sub>c</sub> 1·40 g cm<sup>-3</sup>, Z 4,  $\mu_{Mo}$  2·70 cm<sup>-1</sup>. Crystal size 0·09 by 0·13 by 0·13 mm,  $2\theta_{max}$  50°, min. and max. transmission factors 0·96 and 0·98. The number of reflections was 1133 considered observed out of 2005 unique data, with  $R_{merge}$  0·028 for 54 pairs of equivalent hk0 reflections. Final residuals R,  $R_w$  were 0·038, 0·044 for the observed data. For bpyam. Crystals were grown from ethanol/diethyl ether. C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O, M 199·2, monoclinic, space group  $P 2_1/c$ , a 13·581(2), b 9·926(1), c 16·824(3) Å,  $\beta$  116·481(7)°, V 2030·0(6) Å<sup>3</sup>, D<sub>c</sub> 1·30 g cm<sup>-3</sup>, Z 8,  $\mu_{\rm Cu}$  6·79 cm<sup>-1</sup>. Crystal size 0·10 by 0·18 by 0·43 mm,  $2\theta_{\rm max}$  140°, min. and max. transmission factors 0·81 and 0·94. The number of reflections was 2544 considered observed out of 4236 unique data, with  $R_{\rm merge}$  0·011 for 95 pairs of equivalent reflections. Final residuals R,  $R_w$  were 0·045, 0·055 for the observed data.

For  $[Ni(bpytm)_2]$   $Cl_2.4H_2O$ . Crystals were grown from acetonitrile solution. C<sub>22</sub>H<sub>18</sub>N<sub>6</sub>NiS<sub>2</sub>.2Cl.4H<sub>2</sub>O, M 632·2, triclinic, space group  $P\bar{1}$ , a 9·291(5), b 12·426(7), c 13·425(7) Å,  $\alpha$ 113·54(3),  $\beta$  95·63(3),  $\gamma$  94·43(3)°, V 1403(1) Å<sup>3</sup>,  $D_c$  1·50 g cm<sup>-3</sup>, Z 2,  $\mu_{\rm Mo}$  10·67 cm<sup>-1</sup>. Crystal size 0·03 by 0·20 by 0·20 mm,  $2\theta_{\rm max}$  50°, min. and max. transmission factors 0·81 and 0·97. The number of reflections was 3399 considered observed out of 5247 unique data, with  $R_{\rm merge}$  0·026 for 242 pairs of equivalent reflections. Final residuals R,  $R_w$  were 0·038, 0·046 for the observed data.

For  $[Ni(bpyam)_2]/[BF_4]_2.H_2O$ . Crystals were grown from acetone solution into which low-boiling petroleum was allowed to diffuse slowly. C<sub>22</sub>H<sub>18</sub>N<sub>6</sub>NiO<sub>2</sub>.2BF<sub>4</sub>.H<sub>2</sub>O, *M* 648 · 8, triclinic, space group *P*  $\bar{1}$ , *a* 10 · 663(5), *b* 10 · 861(6), *c* 12 · 799(6) Å,  $\alpha$  $68 \cdot 70(4)$ ,  $\beta$  77 · 84(4),  $\gamma$  78 · 47(4)°, *V* 1338(1) Å<sup>3</sup>, *D<sub>c</sub>* 1 · 61 g cm<sup>-3</sup>, *Z* 2,  $\mu_{Mo}$  8 · 17 cm<sup>-1</sup>. Crystal size 0 · 07 by 0 · 15 by 0 · 15 mm,  $2\theta_{max}$  45°, min. and max. transmission factors 0 · 93 and 0 · 95. The number of reflections was 2619 considered observed out of 3678 unique data, with  $R_{merge}$  0 · 022 for 142 pairs of equivalent reflections. Final residuals *R*,  $R_w$  were 0 · 065, 0 · 087 for the observed data.

For  $[Fe(bpyam)_2]$   $[BF_4]_2$ . Crystals were grown as for  $[Ni(bpyam)_2]$   $[BF_4]_2$ .H<sub>2</sub>O. C<sub>22</sub>H<sub>18</sub>FeN<sub>6</sub>O<sub>2</sub>.2BF<sub>4</sub>, M 627·9, orthorhombic, space group P bcn, a 12·317(6), b 12·609(4), c 16·644(8) Å, V 2585(2) Å<sup>3</sup>,  $D_c$  1·61 g cm<sup>-3</sup>, Z 4,  $\mu_{Mo}$  6·70 cm<sup>-1</sup>. Crystal size 0·10 by 0·10 by 0·15 mm,  $2\theta_{max}$  50°, min. and max. transmission factors 0·91 and 0·95. The number of reflections was 1223 considered observed out of 2595 unique data. Final residuals R,  $R_w$  were 0·069, 0·078 for the observed data.

#### Structure Determinations

Reflection data for each structure were measured at  $21(1)^{\circ}$ C with an Enraf–Nonius CAD-4 diffractometer in  $\theta/2\theta$  scan mode. Data were corrected for absorption by using the analytical method of de Meulenaer and Tompa.<sup>30</sup> Reflections with  $I > 3\sigma(I)$  were considered observed. The structures were determined by direct phasing (MULTAN80<sup>31</sup>) and Fourier methods. Hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by using full-matrix least-squares (BLOCKLS, a local version of ORFLS<sup>32</sup>).

It was clear that for  $[Ni(bpyam)_2]$  [BF<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O one of the BF<sub>4</sub><sup>-</sup> anions was disordered, so refinement was completed (RAELS<sup>33</sup>) with each BF<sub>4</sub><sup>-</sup> ion being included in the refinement as a rigid group with exact  $T_d$  symmetry. A global B–F distance was refined for this structure, the final value being  $1 \cdot 340(3)$  Å. The two disorder components of the group labelled *B* were included, with their occupancies refined, but the sum maintained at 1. The final values of the occupancies were  $0 \cdot 527(6)$  and  $0 \cdot 473$ . Two TLX thermal groups (where T is the translational tensor, L is the librational tensor, and X is the origin of libration) were used to describe the thermal motion of the two anions.

For all structures, reflection weights used were  $1/\sigma^2(F_o)$ , with  $\sigma(F_o)$  being derived from  $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$ . The weighted residual was defined as  $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$ . Atomic scattering factors and anomalous

Table 10. Atomic parameters for bpytm (1)

				-					
Atom	x	y	z	$B_{eq}$	Atom	x	y	z	$B_{eq}$
S	-0.0257(1)	0.6283(1)	0.1556(1)	$4 \cdot 44(2)$	C(5)	0.4207(3)	0.3034(2)	0.5122(2)	$3 \cdot 12(7)$
N(1)	0.4885(3)	0.2955(2)	0.6250(2)	$4 \cdot 48(8)$	C(6)	0.3115(3)	0.4079(2)	0.4856(2)	$3 \cdot 02(7)$
N(2)	0.2461(3)	0.4163(2)	0.3714(2)	3.08(6)	C(7)	0.2829(3)	0.4921(3)	0.5726(2)	$3 \cdot 49(7)$
N(3)	0.1200(3)	0.4192(2)	0.1499(2)	$4 \cdot 84(8)$	C(8)	0.1869(3)	0.5899(3)	0.5407(3)	$3 \cdot 67(8)$
C(1)	0.5967(4)	0.2068(3)	0.6479(3)	$5 \cdot 30(11)$	C(9)	0.1204(3)	0.6004(2)	0.4237(3)	$3 \cdot 63(8)$
C(2)	0.6417(4)	0.1266(3)	0.5638(3)	$4 \cdot 85(10)$	C(10)	0.1524(3)	0.5119(2)	0.3424(2)	$3 \cdot 10(7)$
C(3)	0.5672(4)	0.1343(3)	0.4487(3)	$4 \cdot 45(9)$	C(11)	0.0846(3)	0.5139(3)	$0 \cdot 2125(2)$	$3 \cdot 49(8)$
C(4)	0.4545(3)	$0 \cdot 2233(2)$	$0 \cdot 4224(2)$	3.56(8)					

Table 11. Atomic parameters for bpyam (2)

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Atom	x	y	z	$B_{eq}$	Atom	x	y	z	$B_{eq}$
OA	0.1024(1)	$1 \cdot 0755(1)$	0.4718(1)	$5 \cdot 10(6)$	OB	0.1338(1)	0.5749(1)	0.5485(1)	$4 \cdot 96(6)$
N(1)A	0.1723(1)	0.5595(2)	0.2115(1)	4.08(6)	N(1)B	0.5735(2)	0.1232(2)	0.6482(2)	$7 \cdot 23(9)$
N(2)A	0.1450(1)	0.7839(1)	0.3694(1)	$3 \cdot 49(5)$	N(2)B	0.3236(1)	0.3091(2)	0.5892(1)	$4 \cdot 13(6)$
N(3)A	0.1336(2)	0.8602(2)	0.5196(1)	4.73(7)	N(3)B	0.1043(1)	0.3531(1)	0.5233(1)	$4 \cdot 53(6)$
C(1)A	0.1942(2)	0.4293(2)	0.2051(1)	4.90(8)	C(1)B	0.6040(2)	-0.0015(4)	0.6406(2)	$8 \cdot 59(15)$
C(2)A	0.2198(2)	0.3375(2)	0.2721(2)	$5 \cdot 49(9)$	$C(2)\mathbf{B}$	0.5332(3)	-0.1075(3)	0.6038(3)	$8 \cdot 41(14)$
C(3)A	0.2266(2)	0.3820(2)	0.3520(2)	$6 \cdot 13(10)$	C(3)B	0.4226(2)	-0.0846(3)	0.5719(2)	7.79(13)
C(4)A	0.2055(2)	0.5156(2)	0.3606(1)	5.08(8)	C(4)B	0.3886(2)	0.0442(2)	0.5787(2)	$6 \cdot 32(10)$
C(5)A	0.1767(1)	0.6015(2)	0.2888(1)	3.54(6)	C(5)B	0.4650(2)	0.1451(2)	0.6161(2)	$5 \cdot 39(9)$
C(6)A	0.1457(1)	0.7442(2)	0.2932(1)	$3 \cdot 53(6)$	C(6)B	0.4318(2)	0.2857(2)	0.6234(1)	$4 \cdot 87(8)$
C(7)A	0.1162(2)	0.8300(2)	0.2210(1)	4.76(8)	C(7)B	0.5091(2)	0.3871(3)	0.6639(2)	$6 \cdot 86(11)$
C(8)A	0.0860(2)	0.9608(2)	0.2276(2)	$5 \cdot 22(8)$	C(8)B	0.4729(2)	0.5153(3)	0.6680(2)	$7 \cdot 61(12)$
C(9)A	0.0870(2)	1.0038(2)	0.3056(1)	$4 \cdot 27(7)$	C(9)B	0.3616(2)	0.5403(2)	0.6322(2)	$6 \cdot 04(10)$
C(10)A	0.1164(1)	0.9122(2)	0.3742(1)	$3 \cdot 44(6)$	$C(10)\mathbf{B}$	0.2907(2)	0.4348(2)	0.5932(1)	4.07(7)
$\dot{C(11)}A$	$0 \cdot 1160(2)$	0.9557(2)	$0 \cdot 4597(1)$	$3 \cdot 80(7)$	$C(11)\mathbf{B}$	0.1694(2)	0.4592(2)	0.5529(1)	$3 \cdot 85(7)$

Table 12. Atomic parameters for [Ni(bpytm)<sub>2</sub>] Cl<sub>2</sub>.4H<sub>2</sub>O

Atom	x	y	z	$B_{eq}$	Atom	x	y	z	$B_{eq}$
Ni	$0 \cdot 2240(1)$	0.4541(1)	0.2485(1)	$2 \cdot 71(1)$	N(3)B	0.0222(4)	0.7693(3)	0.4384(3)	$4 \cdot 64(12)$
SA	0.1254(1)	0.3167(1)	0.3210(1)	$3 \cdot 45(3)$	C(1)B	0.4766(4)	0.3031(4)	0.2108(3)	$3 \cdot 66(14)$
N(1)A	0.2875(3)	0.5193(3)	0.1355(2)	$3 \cdot 25(10)$	C(2)B	0.6181(5)	0.2807(4)	0.2303(4)	$4 \cdot 30(16)$
N(2)A	0.1173(3)	0.3273(2)	0.1053(2)	$2 \cdot 81(9)$	C(3)B	0.7137(4)	0.3674(4)	0.3117(4)	4.58(17)
N(3)A	-0.0451(4)	0.1195(3)	0.1979(3)	$4 \cdot 11(12)$	C(4)B	0.6689(4)	0.4746(4)	0.3742(4)	4.05(15)
C(1)A	0.3799(5)	0.6165(4)	0.1561(3)	$4 \cdot 05(14)$	C(5)B	0.5248(4)	0.4908(3)	0.3527(3)	$3 \cdot 09(13)$
C(2)A	0.4161(5)	0.6497(4)	0.0745(4)	$5 \cdot 10(18)$	C(6)B	0.4627(4)	0.5988(3)	0.4167(3)	$2 \cdot 91(12)$
C(3)A	0.3567(6)	0.5800(4)	-0.0316(4)	$5 \cdot 15(18)$	C(7)B	0.5402(4)	0.6966(4)	0.5042(3)	3.75(14)
C(4)A	0.2618(5)	0.4796(4)	-0.0546(3)	4.56(16)	C(8)B	0.4704(5)	0.7907(4)	0.5576(3)	$4 \cdot 34(14)$
C(5)A	0.2278(4)	0.4521(3)	0.0304(3)	$3 \cdot 27(12)$	C(9)B	0.3235(5)	0.7899(3)	0.5239(3)	3.97(13)
C(6)A	0.1240(4)	0.3491(3)	0.0160(3)	$3 \cdot 23(12)$	C(10)B	0.2511(4)	0.6914(3)	0.4364(3)	$2 \cdot 93(12)$
C(7)A	0.0346(5)	0.2810(4)	-0.0826(3)	$4 \cdot 52(15)$	C(11)B	0.0950(4)	0.6815(3)	0.3903(3)	$3 \cdot 15(12)$
C(8)A	-0.0649(5)	0.1906(4)	-0.0855(4)	$5 \cdot 18(17)$	Cl(1)	-0.2833(1)	-0.0712(1)	0.0234(1)	$6 \cdot 27(5)$
C(9)A	-0.0708(5)	0.1676(4)	0.0057(3)	$4 \cdot 25(14)$	Cl(2)	-0.2828(1)	0.7972(1)	0.3283(1)	$5 \cdot 46(4)$
C(10)A	0.0233(4)	0.2367(3)	0.1003(3)	$2 \cdot 98(12)$	Ow(1)	-0.0611(3)	0.0230(2)	0.3571(2)	4.77(10)
C(11)A	0.0294(4)	0.2170(3)	0.2025(3)	$3 \cdot 02(12)$	Ow(2)	$0 \cdot 2109(4)$	-0.0015(3)	0.4290(3)	$7 \cdot 32(15)$
$S\dot{B}$	0.0172(1)	0.5612(1)	0.2801(1)	3.70(3)	Ow(3)	0.4207(5)	-0.0899(4)	0.3082(3)	8.07(17)
N(1)B	0.4309(3)	0.4062(3)	0.2705(2)	3.00(10)	Ow(4)	0.4383(5)	-0.0231(5)	0.1411(4)	10.56(25)
N(2)B	0.3199(3)	0.5974(3)	0.3848(2)	$2 \cdot 84(10)$					( )

Table 13. Atomic parameters for [Fe(bpyam)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>

Atom	x	y	z	$B_{eq}$	Atom	x	y	z	$B_{\mathrm{eq}}$
Fe	0.5000	0.1273(1)	0.2500	$3 \cdot 24(4)$	C(7)	0.1676(6)	0.1777(7)	0.1792(6)	$4 \cdot 39(25)$
0	0.5152(4)	0.0058(4)	0.1581(3)	$4 \cdot 34(16)$	C(8)	0.1484(7)	0.1006(7)	0.1218(6)	5.53(29)
N(1)	0.4015(5)	0.2528(5)	0.3030(4)	$3 \cdot 41(18)$	C(9)	0.2334(7)	0.0331(7)	0.0981(5)	$4 \cdot 71(26)$
N(2)	0.3502(4)	0.1219(4)	0.1904(3)	$2 \cdot 65(15)$	C(10)	0.3314(6)	0.0476(6)	0.1344(5)	$3 \cdot 05(20)$
N(3)	0.4293(5)	-0.0916(5)	0.0639(4)	$4 \cdot 45(20)$	C(11)	0.4323(6)	-0.0160(6)	0.1183(5)	$3 \cdot 36(22)$
C(1)	0.4394(7)	0.3224(7)	0.3565(5)	$4 \cdot 49(25)$	В`́	0.1412(9)	-0.1934(8)	-0.0407(8)	$4 \cdot 52(33)$
C(2)	0.3772(8)	0.4109(7)	0.3811(6)	$5 \cdot 34(30)$	F(1)	0.0809(4)	-0.1168(4)	-0.0012(3)	$5 \cdot 15(14)$
C(3)	0.2790(7)	0.4272(7)	0.3475(6)	4.76(27)	F(2)	0.1006(5)	-0.1973(5)	-0.1178(4)	$8 \cdot 27(22)$
C(4)	0.2387(7)	0.3546(6)	0.2924(5)	3.73(22)	F(3)	0.1208(5)	-0.2913(4)	-0.0081(4)	$8 \cdot 29(22)$
C(5)	0.3031(6)	0.2690(6)	0.2716(4)	$2 \cdot 95(21)$	F(4)	0.2467(4)	-0.1704(4)	-0.0419(4)	6.65(18)
C(6)	0.2702(6)	0.1872(6)	0.2123(5)	3.06(20)					· · · ·

Table 14. Atomic parameters for [Ni(bpyam)<sub>2</sub>] [BF<sub>4</sub>]<sub>2</sub>.H<sub>2</sub>O

Primes indicate disorder of the  $BF_4^-$  ion. The occupancies of the unprimed and primed disorder components are 0.527(6) and

	0.475, respectively										
Atom	x	y	z	$B_{eq}$	Atom	x	y	z	$B_{eq}$		
Ni	0.24679(8)	0.44579(9)	0.26029(8)	$3 \cdot 28(5)$	C(5)B	0.2024(7)	0.5222(7)	0.4611(6)	$3 \cdot 92(11)$		
OA	0.1275(5)	0.2902(5)	0.3222(4)	$4 \cdot 00(8)$	C(6)B	0.1083(7)	0.6138(7)	0.3881(6)	$3 \cdot 60(13)$		
N(1)A	0.4148(5)	0.5345(6)	0.1799(5)	$3 \cdot 68(12)$	C(7)B	0.0166(8)	0.7161(8)	0.4113(7)	$4 \cdot 72(14)$		
N(2)A	0.3665(5)	0.2946(6)	0.2280(5)	$3 \cdot 44(7)$	C(8)B	-0.0604(8)	0.7924(8)	0.3312(8)	$5 \cdot 13(15)$		
N(3)A	0.1229(7)	0.0809(7)	0.3276(7)	$6 \cdot 02(13)$	C(9)B	-0.0468(7)	0.7713(8)	0.2293(8)	$4 \cdot 73(14)$		
C(1)A	0.4299(7)	0.6605(9)	0.1557(7)	$4 \cdot 56(14)$	C(10)B	0.0441(6)	0.6683(7)	0.2119(6)	3.77(11)		
C(2)A	0.5440(9)	0.7105(9)	0.0992(7)	$5 \cdot 36(11)$	C(11)B	0.0763(7)	0.6252(8)	0.1082(6)	3.75(12)		
C(3)A	0.6466(8)	0.6227(11)	0.0698(7)	$5 \cdot 52(20)$	Ow	-0.0894(5)	0.3717(6)	0.1895(5)	$6 \cdot 33(15)$		
C(4)A	0.6334(7)	0.4918(10)	0.0949(6)	$4 \cdot 81(12)$	BA	-0.2638(4)	0.1403(4)	0.4378(4)	$7 \cdot 14(24)$		
C(5)A	0.5140(7)	0.4504(8)	0.1499(5)	$3 \cdot 67(12)$	F(1)A	-0.3097(6)	0.2401(6)	0.3507(5)	$11 \cdot 8(2)$		
C(6)A	0.4891(7)	0.3130(8)	0.1797(6)	3.76(10)	F(2)A	-0.3144(6)	0.1643(6)	0.5348(4)	$12 \cdot 6(2)$		
C(7)A	0.5760(7)	0.2063(10)	0.1607(7)	$5 \cdot 11(14)$	F(3)A	-0.2967(7)	0.0253(6)	0.4426(7)	$15 \cdot 8(4)$		
C(8)A	0.5349(9)	0.0844(10)	0.1930(9)	$6 \cdot 16(23)$	F(4)A	-0.1345(4)	0.1317(7)	0.4231(6)	$13 \cdot 0(3)$		
C(9)A	0.4070(9)	0.0673(8)	0.2438(8)	$5 \cdot 25(13)$	BB	-0.2317(7)	$1 \cdot 0254(7)$	-0.0721(7)	$7 \cdot 0(2)$		
C(10)A	0.3264(7)	0.1771(8)	0.2581(6)	$3 \cdot 85(10)$	F(1)B	-0.2049(10)	$1 \cdot 0913(13)$	-0.1835(8)	$7 \cdot 7(2)$		
C(11)A	0.1835(8)	0.1844(9)	0.3075(7)	$4 \cdot 30(10)$	F(2)B	-0.1925(12)	1.0876(15)	-0.0139(14)	$11 \cdot 1(3)$		
OB	0.1566(5)	0.5232(5)	0.1135(4)	$4 \cdot 22(8)$	F(3)B	-0.3597(8)	$1 \cdot 0224(10)$	-0.0428(9)	$8 \cdot 5(3)$		
N(1)B	0.2774(6)	0.4291(6)	0.4207(5)	$3 \cdot 77(14)$	F(4)B	-0.1699(11)	0.9004(9)	-0.0482(12)	$13 \cdot 9(4)$		
N(2)B	0.1184(5)	0.5944(6)	0.2890(5)	$3 \cdot 36(7)$	BB'	-0.1947(8)	$1 \cdot 0214(9)$	-0.0651(9)	$7 \cdot 4(2)$		
N(3)B	0.0194(6)	0.6928(7)	0.0197(6)	$5 \cdot 44(15)$	F(1)B'	-0.0693(9)	0.9731(13)	-0.0839(12)	$10 \cdot 8(3)$		
C(1)B	0.3639(8)	0.3449(9)	0.4818(7)	$4 \cdot 81(13)$	F(2)B'	-0.2603(12)	0.9233(13)	0.0077(11)	$13 \cdot 4(5)$		
C(2)B	0.3819(10)	0.3487(11)	0.5833(8)	$6 \cdot 80(20)$	F(3)B'	-0.2066(15)	$1 \cdot 1186(16)$	-0.0211(17)	$11 \cdot 4(3)$		
C(3)B	0.3070(11)	0.4420(11)	0.6243(8)	$6 \cdot 88(21)$	F(4)B'	-0.2424(11)	$1 \cdot 0707(14)$	-0.1633(10)	$7 \cdot 5(2)$		
C(4)B	$0 \cdot 2133(10)$	0.5325(9)	0.5637(7)	5.76(22)							

dispersion parameters were from International Tables for X-Ray Crystallography.<sup>34</sup> ORTEP-II<sup>35</sup> running on a Macintosh IIcx was used for the molecular diagrams, and a DEC Alpha-AXP workstation was used for calculations.

Atomic parameters for the structures are listed in Tables 10–14. Material deposited comprises all atom and thermal parameters, interatomic distances, angles and torsional angles and observed and calculated structure factors.\*

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