$^5T_2$–$^1A_1$ Transitions in Six-co-ordinate Iron(II) Complexes of 2,2'-Bi-2-thiazoline and 2,2'-Bi-4,5-dihydrothiazine Ligands

By **Geraldine Bradley, Vickie McKee,** and **S. Martin Nelson,*** Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland
Jane Nelson, The Open University, Milton Keynes MK7 6AA

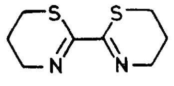
A series of iron(II) complexes of the type $[FeL_2X_2]$ is described [L = a bidentate α-di-imine, 2,2'-bi-4,5-dihydrothiazine (btz) or 2,2'-bi-2-thiazoline (bt) or an alkyl-substituted derivative (bts, btn, and btne); X = NCS^- or $NCSe^-$]. Infrared and electronic spectra together with electrical-conductance measurements characterize the complexes as having neutral (probably *cis*) six-co-ordinate structures in which both the organic ligands and the pseudohalide ions are bound *via* the nitrogen atoms. On the basis of magnetic-susceptibility measurements and of Mössbauer spectra the complexes fall into three classes. The complex $[Fe(btz)_2(NCSe)_2]$ is low spin ($^1A_1$ ground state) between 90 and 300 K. Complexes of the ligands btn and btne which bear alkyl substituents adjacent to the donor atoms are high spin ($^5T_2$ ground state) in this temperature range. The remaining four complexes exhibit a $^5T_2$–$^1A_1$ spin transition between 90 and 300 K. The transition is very abrupt in some cases and hysteresis effects are also observed. The electronic spectra of the corresponding nickel(II) complexes indicate a correlation between the apparent Dq(Ni) values and the ground state of the iron(II) complexes.

We have recently described[1] the preparation and properties of a range of metal complexes of the nitrogen–sulphur ligands 2,2'-bi-4,5-dihydrothiazine (btz) and 2,2'-bi-2-thiazoline (bt) and some of the methyl-substituted derivatives (bts and btn) of the latter. The properties indicated that, in the case of all the metal complexes examined, the ligands are bidentately co-ordinated *via* the α-di-imine group. Among the complexes described were the low-spin octahedral ions $[Fe(ligand)_3]^{2+}$. In this paper we report the results of a magnetic and Mössbauer-effect investigation of a series of six-co-ordinate bis(ligand)iron(II) complexes

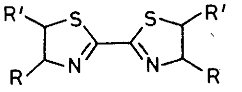
---

[1] J. Nelson, S. M. Nelson, and W. D. Perry, *J.C.S. Dalton*, 1976, 1282.

in which the co-ordination sphere is completed by *N*-bonded $[NCS]^-$ or $[NCSe]^-$ ions. These complexes were of particular interest in view of the observation that several of them react with dioxygen in solution to give, amongst other, products whose properties appear to be consistent with the presence of co-ordinated dioxygen.[2] The examination of the parent iron(II) complexes described here was undertaken as a desirable preliminary to the fuller understanding of the reactions with dioxygen. It was also of interest to compare their properties with those of analogous complexes of structurally similar α-di-imines such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) known to exhibit spin quintet–singlet equilibria at temperatures below ambient.[3]



btz



bt, R = R′ = H

bts, R = H, R′ = Me

btn, R = Me, R′ = H

btne, R = Et, R′ = H

TABLE 1

Analytical, magnetic, and Mössbauer data for the iron(II) complexes

Complex	Analysis (%) Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	$\mu_{eff.}$ [a]/B.M. 293	93 K	δ [b,c]/mm s^{-1} 293	77 K	ΔE_Q [c]/mm s^{-1} 293	77 K
$[Fe(btz)_2(NCS)_2]$	37.9	4.1	14.5	37.7	4.2	14.7	5.01	1.68	0.95	0.41	2.08	0.59
$[Fe(btz)_2(NCSe)_2]$	34.8	3.9	12.4	32.5	3.6	12.6	0.50	0.45	0.25	0.30	0.44	0.52
$[Fe(bt)_2(NCS)_2]$	32.6	3.2	16.3	32.6	3.1	16.3	5.10	1.05	0.96	0.34	2.73	0.55
$[Fe(bt)_2(NCSe)_2]$	27.5	2.6	13.6	27.5	2.6	13.7	5.40	1.31	0.99	0.37	2.72	0.39
$[Fe(bts)_2(NCS)_2]$	37.8	4.2	14.8	37.7	4.2	14.7	5.26	0.84	0.96	0.36	2.70	0.59
$[Fe(btn)_2(NCS)_2]$	37.5	4.1	14.6	37.7	4.2	14.7	5.27	5.21	1.00	1.12	1.43	2.26
$[Fe(btne)_2(NCS)_2]$	41.2	4.8	12.5	42.0	5.1	13.4	5.27	5.13	1.07	1.13	1.44	1.90

[a] Corrected for diamagnetism of ligands. [b] Relative to natural iron. [c] Estimated error ±0.02 mm s^{-1}.

RESULTS AND DISCUSSION

The complexes examined are listed in Table 1 together with analytical and selected physical data. They were prepared, in most cases, by reaction of an iron(II) salt in dry ethanol with twice the stoicheiometric amounts of the organic ligand and pseudohalide ion in the absence of air. Failure to exclude oxygen resulted in products which were mixtures of the desired complex with a second complex believed [2] to contain bound O_2. In the preparation of $[Fe(btz)_2(NCS)_2]$ particular difficulty was encountered in obtaining a pure product, and an alternative procedure was to displace pyridine from the complex $[Fe(py)_4(NCS)_2]$ by reaction with an excess of btz in oxygen-free ethanol under N_2. This method was unsatisfactory in other cases because of incomplete displacement of pyridine. Mössbauer spectra were a convenient method of monitoring the purity of the products. None of the solid complexes react with O_2 and once isolated they could be stored indefinitely without apparent change. The complexes are poorly soluble in most organic solvents and are decomposed by water.

The inference from the stoicheiometry that the complexes have neutral six-co-ordinate structures is supported by the electronic and vibrational spectra and by electrical-conductance measurements. Thus, all the complexes are non-electrolytes ($\Lambda < 1.0$ S cm^2 mol^{-1}) in 5×10^{-4} mol dm^{-3} $C_2H_4Cl_2$ solution. Moreover, there is a fair correspondence between the electronic spectra of the solids and of their solutions in the same solvent. The visible spectra (Table 2) consist of a rather intense, usually double-peaked, absorption band in the 16 000—18 500 cm^{-1} region. Molar absorption coefficients are in the range 1 000—4 000 dm^3 mol^{-1} cm^{-1}. The spectral bands are thus very similar in energy to, but less intense than, those occurring in the low-spin tris(ligand) complex ions and we attribute them also to charge transfer of metal t_{2g} electrons to vacant p_{π^*} orbitals of the chelate rings. Those complexes which are high spin at room temperature also showed a very weak poorly resolved absorption in the 11 000 cm^{-1} region which may be due to a *d–d* transition ($^5T_{2g} \rightarrow {}^5E_2$ in O_h symmetry).

TABLE 2

Electronic spectra * of the iron(II) complexes

Complex		
$[Fe(btz)_2(NCS)_2]$	Mull	17.6, 16.8
	$C_2H_4Cl_2$	18.2 (3 770), 16.1 (sh)
$[Fe(btz)_2(NCSe)_2]$	Mull	17.7, 16.1
	$C_2H_4Cl_2$	18.2 (sh), 16.3 (2 750)
$[Fe(bt)_2(NCS)_2]$	Mull	17.9, 16.3
	$C_2H_4Cl_2$	17.9 (2 880), 16.2 (sh)
$[Fe(bt)_2(NCSe)_2]$	Mull	18.2, 16.5
	$C_2H_4Cl_2$	18.2 (sh), 16.4 (3 360)
$[Fe(bts)_2(NCS)_2]$	Mull	17.9, 16.2
	$C_2H_4Cl_2$	17.8 (2 400), 14.4 (sh)
$[Fe(btn)_2(NCS)_2]$	Mull	18.6, 16.7
	$C_2H_4Cl_2$	17.7 (1 660), 16.0 (sh)
$[Fe(btne)_2(NCS)_2]$	Mull	17.7, 16.1
	$C_2H_4Cl_2$	17.7 (1 480), 16.0 (sh)

* Absorption maxima in 10^3 cm^{-1}; absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) for solution spectra are given in parentheses.

Infrared Spectra.—The asymmetric stretching mode

---

[2] V. McKee, S. M. Nelson, and J. Nelson, *J.C.S. Chem. Comm.*, 1976, 225.

[3] H. A. Goodwin, *Co-ordination Chem. Rev.*, 1976, **18**, 293 and refs. therein.

(ν_{asym}) of [NCS]$^-$ and [NCSe]$^-$ in the complexes occurs as a strong rather broad absorption at *ca.* 2 060—2 080 cm^{-1} (Table 3). The energy of the absorption as well as its intensity suggest co-ordination *via* the nitrogen atom. Except for the single low-spin (at room temperature) complex [Fe(btz)$_2$(NCSe)$_2$], the ν_{asym} mode is split by *ca.* 10—15 cm^{-1}, a fact which suggests that, in common with most known [Fe(diamine)$_2$X$_2$] complexes, the co-ordinated anions are in a *cis* configuration. The symmetric stretching mode (ν_{sym}), usually of low intensity, could not be identified with certainty.

The spectra of the co-ordinated thiazine and thiazoline ligands are slightly altered from those of the free ligands. The most noticeable effect is in the region of the ν(C=N) stretching mode which is shifted 20—50 cm^{-1} to lower wavenumbers on co-ordination (Table 3), but retains the high intensity which makes it the significant feature of this part of the spectrum. When co-ordination results in the formation of a low-spin iron(II) complex, as in [Fe(btz)$_2$(NCSe)], this mode 'disappears,' a radical alteration in intensity or position (or both) making it difficult to identify.[1,4]

TABLE 3

Infrared data (cm^{-1}) for the iron(II) complexes

Complex	ν_{asym}(NCS)	ν(C=N)	$\Delta\nu$(C=N) [a]	ν(Fe–N) [b]
[Fe(btz)$_2$(NCS)$_2$]	2 070, 2 083	1 568	46	233
[Fe(btz)$_2$(NCSe)$_2$]	2 058			
[Fe(bt)$_2$(NCS)$_2$]	2 073, 2 085 (sh)	1 568	27	225 (sh), 254
[Fe(bt)$_2$(NCSe)$_2$]	2 071, 2 083 (sh)	1 570	25	227 (sh), 250br
[Fe(bts)$_2$(NCS)$_2$]	2 073, 2 082 (sh)	1 555	38	243br
[Fe(btn)$_2$(NCS)$_2$]	2 067, 2 082 (sh)	1 562	30	250br
[Fe(btne)$_2$(NCS)$_2$]	2 058, 2 070 (sh)	1 565	19	226br

[a] Downfield shift relative to the position of this mode in the free ligand. [b] Fe–N(NCS) and/or Fe–N(ligand) stretch (see text).

The strong absorptions occurring at *ca.* 800—1 000 cm^{-1} in the free ligand and originating in the skeletal vibrations of the heterocyclic ring are shifted somewhat on co-ordination. Once again the low-spin (at 293 K) complex [Fe(btz)$_2$(NCSe)$_2$] differs from all the others in that the shifts are larger.

In the low-frequency i.r. region a band at *ca.* 250 cm^{-1}, absent in the spectra of the free ligands, was observed in all the spectra except that of the low-spin complex already referred to. This band is asymmetrical to the low-energy side or is resolved into a second band at *ca.* 230 cm^{-1} (Table 3). These absorptions are probably due to metal–nitrogen stretching modes but we do not have sufficient information to decide which band corresponds mainly to ν(Fe–NCX) and which to ν(Fe–ligand). However, we note that studies[5] on analogous 2,2′-bipyridine and 1,10-phenanthroline complexes using isotopically enriched ^{57}Fe and ^{54}Fe samples have indicated that the lower-frequency component is generally the metal–ligand stretch. The absence of absorption at 230—250 cm^{-1} in low-spin [Fe(btz)$_2$(NCSe)$_2$] is evidence in support of the assignment of the low-frequency band to ν(Fe–N) vibrations in the high-spin cases since it has been demonstrated in other systems that a change from a quintet to a singlet ground state leads to large shifts to higher wavenumbers of both ν(Fe–N) vibrations;[5,6] this is considered to be a result of bond contraction on spin pairing.[7]

The data considered so far are sufficient to establish neutral six-co-ordinate (probably *cis*) configurations in which all the donor atoms are nitrogen for all the complexes.

Magnetic Properties.—Magnetic susceptibilities of the complexes were measured within the range 90—300 K. The complexes fall into three classes on the basis of these measurements (see Table 1). The complex [Fe(btz)$_2$(NCSe)$_2$] has a moment of only *ca.* 0.5 B.M.* at 293 and 93 K, unequivocally establishing the occurrence of a ${}^1A_1$ ground state. The two complexes [Fe(btn)$_2$(NCS)$_2$] and [Fe(btne)$_2$(NCS)$_2$] which contain sterically hindered ligands, *i.e.* those with alkyl substituents α to the donor atoms, are high spin ($\mu_{\mathrm{eff.}}$ 5.1—5.3 B.M.) over the entire temperature range investigated. Clearly, these have ${}^5T_2$ ground states. The remaining four complexes exhibit temperature-dependent magnetic moments. As shown in the Figure, the moments decrease from values (5.0—5.4 B.M.) at 293 K appropriate to high-spin Fe$^{\mathrm{II}}$ to values at *ca.* 90 K which approach that of fully spin-paired Fe$^{\mathrm{II}}$. In two cases (see Figure) the moments appear to level off to values somewhat in excess of that (*ca.* 0.6 B.M.) expected. It is possible that this is due to the presence of some high-spin iron(II) or iron(III) impurity although no evidence for this was apparent in any of the Mössbauer spectra. Alternatively, or additionally, the higher than expected residual paramagnetism may arise from a fraction of the molecules remaining permanently in the high-spin state as observed in several other systems.[3,8]

For the two complexes of the unsubstituted ligand bt the change in magnetic properties with temperature is particularly abrupt, being largely complete over a temperature interval of a few degrees. Hysteresis effects were also noted for these two complexes in that the temperature of the onset of the transition was dependent on the rate of cooling (or heating). Thus, a

---

* Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

[4] W. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 4834.

[5] J. H. Takemoto and B. Hutchinson, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 769; *Inorg. Chem.*, 1973, **12**, 705.

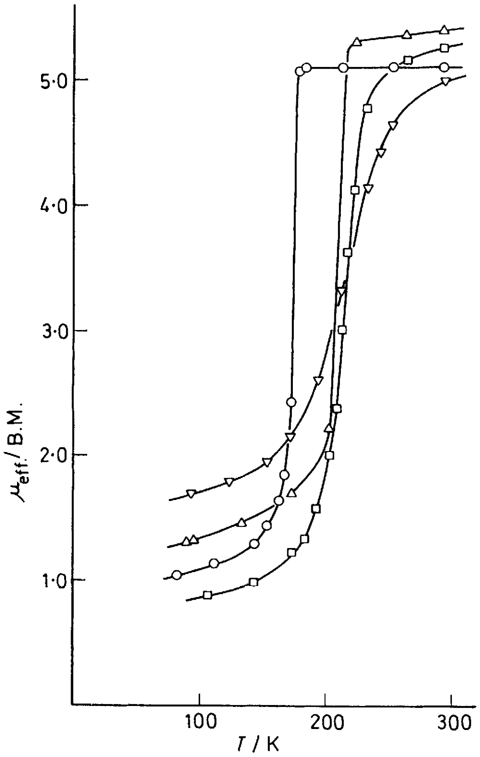
[6] K. Nakamoto, *Angew. Chem.*, 1972, **84**, 755.

[7] E. König and K. J. Watson, *Chem. Phys. Letters*, 1970, **6**, 457.

[8] E. König, *Co-ordination Chem. Rev.*, 1968, **3**, 471.

rapid rate of approach (> *ca.* 5° min^{-1}) to the transition temperature from either direction produced an overshoot of up to 10—15° in the initiation of the transition. These observations, which have been noted [3,8] also in other systems, are strongly indicative of co-operative effects arising from phase changes in the solid, these, in turn, having their origin in the bond contraction which accompanies the spin-pairing process.[7]

Mössbauer Spectra.—The conclusions based on the magnetic data with regard to the spin state of Fe^{II} in the various complexes and to the $^5T_2$–$^1A_1$ spin transitions are amply confirmed by measurements of the Mössbauer spectra at 293 and 77 K. Isomer shifts, δ (relative to natural iron), and quadrupole splittings, ΔE_Q, are given in Table 1. In each case where magnetic measurements indicate a spin-singlet ground state, at whatever temperature, the isomer shifts fall within the narrow range 0.25—0.4 mm s^{-1} and the quadrupole splittings within the range 0.4—0.6 mm s^{-1} characteristic of this spin state.[9] Bancroft *et al.*[10] predicted that the critical isomer-shift value (for $^1A_1$ complexes) for magnetic cross-over should be in the range 0.3—0.4 mm s^{-1}, a prediction that has been confirmed by data [11] for iron(II)-diphosphine complexes. In accord with this conclusion we find that in the present series of complexes the only one having a δ value lower than 0.3 mm s^{-1} is $[\text{Fe(btz)}_2(\text{NCSe})_2]$ which does not exhibit a spin cross-over. Again, where the magnetic measurements indicate a $^5T_2$ ground state, the isomer shifts fall in the range 0.95—1.15 mm s^{-1} typical of high-spin Fe^{II}. Although the variation in δ (at 293 K) from one complex to another is small there is a rough inverse correlation of the magnitude of δ with Dq(Ni), the average octahedral ligand-field splitting of the corresponding nickel(II) complexes (see later). This is the expected effect since isomer shifts decrease with increases in both ligand σ-donor and π-acceptor properties. The quadrupole splittings observed for the high-spin complexes are again typical of this class of complex.[9] The values fall in the range 2.0—2.7 mm s^{-1} except for the two complexes which do not undergo spin pairing at temperatures down to 90 K. Since these contain ligands bearing substituents α to the nitrogen donors it seems reasonable to associate the smaller ΔE_Q values to sterically induced distortions.



Temperature dependence of the magnetic moments of $[\text{Fe(bt)}_2(\text{NCSe})_2]$ (△), $[\text{Fe(bts)}_2(\text{NCS})_2]$ (□), $[\text{Fe(bt)}_2(\text{NCS})_2]$ (○), and $[\text{Fe(btz)}_2(\text{NCS})_2]$ (▽). The data refer to cooling curves in which the rate of cooling was *ca.* 0.2° min^{-1}

The Nickel(II) *Complexes*.—The iron(II) complexes described extend the number of examples of that already extensive class of iron(II) complex having α-di-imine and related ligands known to exhibit $^5T_2$–$^1A_1$ spin cross-over behaviour at accessible temperatures.[3] The important condition [12] for the occurrence of near equi-energetic ground states is $10Dq_{(\text{h.s.})} < \pi < 10Dq_{(\text{l.s.})}$ where π is the mean pairing energy for the metal *d* electrons. Because the ligand-field splitting parameters are not easily obtained from the spectra of iron(II) complexes, we evaluated $10Dq$(Ni) of the corresponding nickel(II) complexes. For cationic $[\text{ML}_3]^{2+}$ and $[\text{ML}_2]^{2+}$ complexes (L = a bi- or tri-dentate amine) it has been shown that for Dq(Ni) values in excess of *ca.* 1 170 cm^{-1} the corresponding iron(II) complexes are low spin, while for Dq(Ni) values lower than *ca.* 1 160 cm^{-1} the corresponding iron complexes are high spin.[13] Relevant data for the nickel(II) complexes are in Table 4. No splitting of the lowest-energy spin-allowed bands in the electronic spectra was observed and we therefore take this band as a measure of $10Dq$, on the assumption of approximate octahedral symmetry. With one exception, *X*-ray powder-diffraction patterns of the two series of complexes were either identical or very similar for all the corresponding pairs and we therefore assume that they have closely similar structures. It may be significant that $[\text{Fe(btz)}_2(\text{NCSe})_2]$, the only complex with a $^1A_1$ ground state at room temperature, has a distinctly different pattern from its nickel(II) analogue, an observation at least consistent with the occurrence of a phase change on spin pairing in these complexes.

While the variation in $10Dq$(Ni) among the various

---

[9] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[10] G. M. Bancroft, M. J. Mayo, and B. E. Prater, *J. Chem. Soc.* (*A*), 1970, 956.

[11] W. Levason, C. A. McAuliffe, M. M. Khan, and S. M. Nelson, *J.C.S. Dalton*, **1975**, 1778.

[12] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.*, 1964, **A280**, 235.

[13] S. M. Nelson and J. Rodgers, *J. Chem. Soc.* (*A*), 1968, 272; see also M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, 1963, **2**, 1178.

complexes is small (600 ± 100 cm^{-1}) there is a definite correlation with the spin state of the corresponding iron(II) complexes. The highest value (10 800 cm^{-1}) is found for $[Ni(btz)_2(NCSe)_2]$, the corresponding iron(II) complex being low spin at all temperatures investigated, while the lowest values of $10Dq$(Ni) refer to the two complexes of the alkyl-substituted ligands whose iron(II) analogues are high spin even at 77 K. Intermediate values of $10Dq$(Ni) are associated with $^5T_1$–$^1A_1$ cross-over. However, the critical cross-over value for $10Dq$(Ni) of *ca.* 10 500 cm^{-1} is much lower for this series of neutral mixed-ligand complexes than previously found[13] for the octahedral cationic polyamine complexes referred to above.

TABLE 4

Analytical and selected physical data for the nickel(II) complexes

	Analysis (%)								
	Found			Calc.					
Complex	C	H	N	C	H	N	$\mu_{eff.}$ [a]/ B.M.	ν_1 [b]/ 10^3 cm^{-1}	Isomorphous with iron(II) analogue
$[Ni(btz)_2(NCS)_2]$	37.6	4.1	14.4	37.6	4.2	14.6	3.13	10.5	Yes
$[Ni(btz)_2(NCSe)_2]$	32.7	3.7	12.1	32.3	3.6	12.5	3.14	10.8	No
$[Ni(bt)_2(NCS)_2]$	32.4	3.1	16.3	32.2	3.1	16.1	3.11	10.6	Yes
$[Ni(bt)_2(NCSe)_2]$	27.0	2.6	13.6	27.4	2.6	13.7	3.04	10.6	Yes
$[Ni(bts)_2(NCS)_2]$	36.9	4.1	13.9	37.2	4.2	14.6	3.19	10.5	Yes
$[Ni(btn)_2(NCS)_2]$	37.0	4.1	14.5	37.2	4.2	14.6	3.21	10.3	No [c]
$[Ni(btne)_2(NCS)_2]$	39.7	4.7	13.3	41.8	5.1	13.3		10.2	No [c]

[a] At 293 K; corrected for diamagnetism of ligands. [b] Energy of the lowest-energy *d–d* band in the electronic spectrum, assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition. [c] Very similar although not identical *X*-ray powder patterns.

EXPERIMENTAL

The ligands btz, bt, bts, and btn were prepared by the method of Tomalia and Paige[14] modified as described earlier.[1] The new ligand btne was analogously prepared from dithio-oxamide and 2-aminobutan-1-ol.

The complexes were prepared by reaction of ethanolic solutions of MX_2 (Fe or Ni; X = NCS or NCSe) (1 mmol), prepared *in situ* by metathesis from the metal chloride and sodium pseudohalide, with the appropriate ligand (2 mmol) also in ethanol solution at *ca.* 70 °C. All the solutions were deoxygenated and all the operations were carried out under N_2. The products separated immediately or within a few minutes, except for those of btn and btne which were recovered after partial removal of solvent. The complexes were washed with dry oxygen-free ethanol and dried *in vacuo*. Samples of $[Fe(btz)_2(NCS)_2]$, which has a high affinity for O_2, were invariably contaminated with oxygenation or oxidation products when prepared by this method. An improved procedure was to displace pyridine from $[Fe(py)_4(NCS)_2]$ in oxygen-free ethanol by addition of an excess of btz. Separate experiments showed that the effect of pyridine is to drastically diminish the rate of uptake of O_2 by $[Fe(btz)_2(NCS)_2]$.

X-Ray diffraction patterns on powdered samples were obtained using a Phillips wide-angle goniometer and associated recording equipment. Other physical measurements were carried out as described earlier.[1]

We thank the Department of Education for N. Ireland for the award of support grants (to G. B. and V. McK.), and the Open University for a research grant (to J. N.).

[7/1474 *Received*, 15*th August*, 1977]

---

[14] D. A. Tomalia and J. N. Paige, *J. Org. Chem.*, 1973, **38**, 3949.