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Metal Complexes of 1,10-Phenanthroline Derivatives. IX* $^5T_2 \rightleftharpoons {}^1A_1$ Spin Transitions in Iron(II) Complexes of 2-(1,10-Phenanthrolin-2-yl)thiazole Derivatives

Harold A. Goodwin,[A] *Dennis W. Mather*[A,B] *and Frank E. Smith*[C]

[A] School of Chemistry, University of New South Wales,
P.O. Box 1, Kensington, N.S.W. 2033.
[B] Commonwealth Postgraduate Scholar.
[C] School of Chemical Sciences, Universiti Sains Malaysia, Penang.

Abstract

The preparation of the tridentate chelating agents 2-(1,10-phenanthrolin-2-yl)thiazole, 2-(1,10-phenanthrolin-2-yl)-4-(2-pyridyl)thiazole, 2-(1,10-phenanthrolin-2-yl)thiazolidine and 2-(1,10-phenanthrolin-2-yl)benzothiazole is described. Data from the spectra of the bis-ligand nickel complexes indicate that the ligands all have field strengths in the iron(II) crossover region. The temperature dependence of the magnetism of the bis-ligand iron(II) complexes reveals that, except for the complexes of the pyridylthiazole, a smooth, temperature-induced $^5T_2 \rightleftharpoons {}^1A_1$ transition occurs in these compounds. For no complex is the transition complete within the experimental temperature range (83–363 K). The complex of the pyridylthiazole is high-spin throughout the range, the uncoordinated pyridyl group hindering the close approach of ligand and metal atom necessary for spin-pairing. The ability of the other ligands to induce a spin transition is primarily a consequence of distortions in the environment about the metal atom arising from coordination of the five-membered thiazole or related ring.

Introduction

Among the many systems found to induce a spin transition in iron(II) those containing a donor atom in a five-membered heterocycle linked to a pyridine ring occur with notable frequency. Thus the bidentate chelating agents 2-(2-pyridyl)imidazole,[1,2] 2-(2-pyridyl)imidazoline,[3] 2-(2-pyridyl)benzimidazole,[4] and 3-phenyl-5-(2-pyridyl)-pyrazole[5] all effect a spin transition in iron(II), while in the tridentate series 2-(2-pyridylamino)-4-(2-pyridyl)thiazole and its derivatives,[6,7] 2,4-bis(2-pyridyl)thiazole,[8,9] and 2,6-di(benzothiazol-2-yl)pyridine[10] do the same. These bidentate and tridentate chelating agents may be considered to be derivatives of 2,2′-bipyridine and 2,2′,2″-terpyridine, respectively, both of which effect spin-pairing in iron(II). Replacement of one of the six-membered rings in these parent substances by a five-membered ring

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* Part VIII, *Aust. J. Chem.*, 1974, **27**, 2121.

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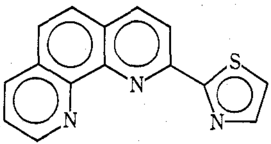
must introduce substantial distortions from normal bond angles about the metal atom and it has been already suggested[11] that the introduction of low-symmetry components into the ligand field will suppress to some extent the energy barrier between the high-spin and low-spin states of iron(II).

As part of a general investigation of the influence of the nature of a donor substituent in the 2-position of 1,10-phenanthroline on the electronic properties of the derived complexes, particularly with iron(II), we have examined the behaviour of derivatives containing a five-membered heterocyclic substituent. Such derivatives are related to the tridentate chelating agents mentioned above. Derivatives containing a thiazole or related ring system (1)–(4) are reported in the present work.



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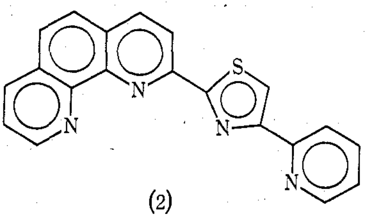

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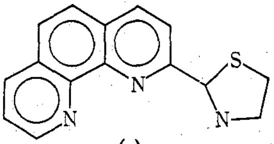

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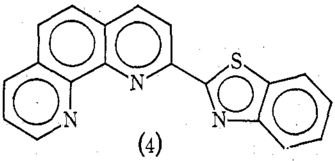

(4)

Results and Discussion

The Ligands

2-(1,10-Phenanthrolin-2-yl)thiazole (1) and 2-(1,10-phenanthrolin-2-yl)-4-(2-pyridyl)thiazole (2) were prepared from 1,10-phenanthroline-2-carbothioamide[12] by an adaptation of the general Hantzsch thiazole synthesis using methods essentially the same as those employed in the preparation of the corresponding pyridine derivatives.[13,14] 2-(1,10-Phenanthrolin-2-yl)thiazolidine (3) and 2-(1,10-phenanthrolin-2-yl)benzothiazole (4) were prepared by reaction of 1,10-phenanthroline-2-carbaldehyde with 2-aminoethanethiol and *o*-aminobenzenethiol, respectively. In the preparation of (4) the corresponding benzothiazoline is formed initially. This compound is highly sensitive to oxidation, even in the solid state, and could not be isolated pure. To ensure complete oxidation of the benzothiazoline intermediate the reaction mixture was aerated for about 30 h, as in the preparation of the corresponding pyridine derivative.[15] The complete conversion to the benzothiazole was confirmed by the appearance of a peak at m/e 313 in the mass spectrum of the product and the absence of any peak at m/e 315. Moreover, no bands which could be ascribed to N–H or S–H vibrations were observed in the infrared spectrum of the final product.

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The other ligands, (1), (2), (3), showed the expected parent ion peaks at m/e 263, 340 and 267, severally, in their mass spectra.

Each of the molecules functions as a planar tridentate chelating agent. Although it is stereochemically feasible for coordination to involve either a N–N–N or N–N–S sequence of donor atoms, the former is believed to apply because of the relatively poor donor capacity of heterocyclic sulphur and the reported nitrogen-coordination of thiazole and certain of its derivatives.[13,16] The ligands thus belong to the ter-imine group and spin transitions in iron(II) complexes of such ligands are already well recognized.[6,8,10,17]

It should be pointed out that, although (2) might appear to be capable of functioning as a quadridentate chelating agent, molecular models indicate that this would be extremely unlikely because of the gross distortions that would be introduced into the metal ion environment. It is therefore expected that (2) would function as a tridentate chelating agent with the pyridine ring being rotated out of the plane of the remainder of the molecule in much the same manner as has been postulated for the ligand molecules in the bis(2,2′,2″,2‴-quaterpyridine)iron(II) ion.[18]

All the chelating agents yielded complexes of the type bis[2-(1,10-phenanthrolin-2-yl)thiazole]metal(II) fluoroborate, $[ML_2][BF_4]_2$, when they were allowed to react with either iron(II) or nickel(II) fluoroborate in ethanolic solution. Other salts containing $[FeL_2]^{2+}$ (L = (2)) were obtained from the mono complex $[FeLCl_2]$ by reaction in water in which it disproportionates, followed by addition of the appropriate sodium salt. Satisfactory analyses for carbon, hydrogen and metal content were obtained for all the complexes.* The complexes are listed in Table 1 together with relevant data. Infrared spectra of the complex fluoroborates showed that these are ionic and this was confirmed by the conductivity of the complexes in suitable solvents, indicating that they are bi-univalent electrolytes.

Table 1. Data for the complexes $[ML_2]X_2,nH_2O$

Λ, conductivity (S cm^2) of 10^{-3}M solutions, in dimethylformamide except where stated

M	L	X	n	Colour	μ at 83 K	μ at 303 K	θ (K)	Λ
Fe	(1)	BF_4	2	purple	1·60	3·01	—	128
Ni	(1)	BF_4	4	pale green	—	3·20	—	125
Fe	(2)	I	3	red brown	5·0	5·2	−7	130
Fe	(2)	Br	4	red brown	5·3	5·4	−1	130
Fe	(2)	BF_4	3	red brown	5·1	5·2	0	126
Fe	(2)	NO_3	4	tan	5·4	5·4	0	133
Ni	(2)	BF_4	4	tan	3·3	3·4	−6	132
Fe	(3)	BF_4	1	brown	4·2	4·7	—	34[A]
Ni	(3)	BF_4	0·5	grey	3·0	3·1	−8	35[A]
Fe	(4)	BF_4	1	violet	1·6	2·8	—	131
Ni	(4)	BF_4	0	brown	3·1	3·2	−7	48[A]

[A] In nitrobenzene at 298 K.

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* Copies of a table giving the analytical data are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 372 Albert Street, East Melbourne, Vic. 3002.

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Magnetism of the Iron Complexes

At room temperature $[FeL_2][BF_4]_2$ (L = (1)) has a magnetic moment (3·0 B.M.) intermediate between that expected for iron(II) in the $^5T_2$ state and that for the metal in the $^1A_1$ ground state. The temperature dependence of this moment (Fig. 1, Table 2) indicates that a gradual temperature-induced $^1A_1 \rightleftharpoons {}^5T_2$ transition occurs in this substance. Within the experimental temperature range this transition is incomplete but it is obvious from Fig. 1 that it would continue above the upper temperature limit. On the other hand, the curve of μ against T reveals that there would not be expected to be any further significant lowering of the moment beyond the lower limit. As in most other iron(II) systems displaying a spin transition[19] this residual paramagnetism presumably arises from a fraction of molecules permanently in the $^5T_2$ state and necessary for the stability of the particular crystal lattice. It

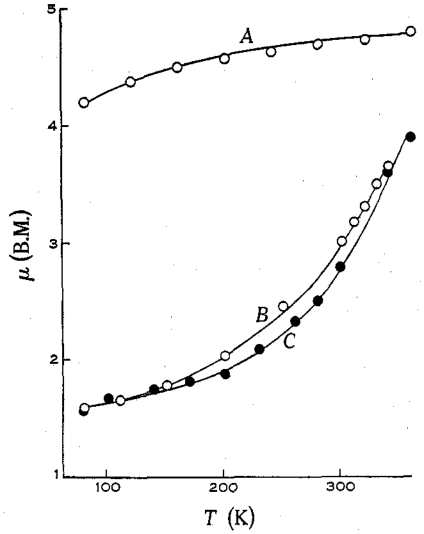

Fig. 1. Temperature dependence of the magnetic moment of $[FeL_2][BF_4]_2$. *A*, L = (3); *B*, L = (1); *C*, L = (4).

Table 2. Detailed magnetic data for the complexes $[FeL_2][BF_4]_2$
T in K, χ and Δ in m^3 mol^{-1}, μ in B.M.

T	$10^{10}\chi'_M$	μ	T	$10^{10}\chi'_M$	μ	T	$10^{10}\chi'_M$	μ
L = (1), $10^{10}\Delta = -54$			L = (4), $10^{10}\Delta = -58$			L = (3), $10^{10}\Delta = -54$		
83	483	1·60	83	466	1·58	83	3320	4·20
113	379	1·66	103	426	1·68	123	2430	4·38
153	327	1·79	143	336	1·75	163	1930	4·50
203	321	2·05	173	299	1·82	203	1600	4·57
253	377	2·47	203	273	1·89	243	1370	4·62
303	468	3·01	233	292	2·09	283	1210	4·69
313	502	3·18	263	324	2·34	323	1080	4·73
323	527	3·31	283	349	2·51	363	989	4·80
333	577	3·50	303	408	2·81			
343	610	3·66	343	587	3·60			
			363	659	3·92			

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[19] König, E., *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 975.

can be seen from Fig. 1 that the temperature dependence of the magnetic moment of $[FeL_2][BF_4]_2$ (L = (4)) almost parallels that of the complex of the thiazole (1). In both of these complexes the spin transition is continuous over the experimental temperature range, this being the more usual behaviour observed for iron(II) crossover systems. The magnetic moment of $[FeL_2][BF_4]_2$ (L = (3)) is only slightly temperature dependent but at the lower extremity of the range studied a significant decrease in moment is observed. This suggests that in this complex also the $^1A_1$ state for iron is becoming accessible as the temperature is lowered. This is further supported by the observation that in nitromethane solution at 290 K this complex has a magnetic moment of 2·9 B.M. Undoubtedly in solution there is a much greater fraction of $^1A_1$ ground state molecules. The difference between the values obtained for the magnetism of the one complex in the solid and solution states clearly reflects the importance of the role of crystal lattice forces in deciding the course of a spin transition. An additional component to the ligand field about the metal atom will be provided by the packing in the lattice. In the present system a negative contribution from the lattice is evident, but in other iron(II) crossover systems a positive contribution has been observed.[7,20]

The complex of the pyridylthiazole (2) behaves as a simple paramagnet and its magnetism follows the Curie–Weiss law

$$\chi'_M = C/T-\theta$$

with a small value of θ (listed in Table 1). Since it is known that the anion associated with a complex cation can influence the properties of a crossover system, several salts containing the cation $[FeL_2]^{2+}$ (L = (2)) were prepared. In all instances, however, the complexes were found to be high-spin, and no significant temperature dependence of the magnetic moment was observed.

Nickel Complexes

Nickel complexes, $[NiL_2][BF_4]_2$, were prepared for each of the ligands so as to obtain from spectral information an estimate of the relative field strengths of the ligands. The spectra all show a well defined peak at about 11600 cm^{-1} which can be ascribed to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition in an essentially octahedral field. Even if the symmetry of the ligand field is considerably lower than O_h, as in fact is expected to be the case, use of these spectral data to obtain *relative* values of the ligand field strength remains valid since all four ligands are structurally closely related. For (1), (2), (3) and (4) absorption maxima are observed at 11630, 11630, 11550 and 11700 cm^{-1}, severally, giving the following order of field strengths:

$$(4) > (1) \approx (2) > (3)$$

If the extent of conjugation in the ligand is significant in determining the effective field strength then the intermediate value of the thiazoles is to be expected. All four ligands have field strengths which are lower than that of terpyridine and which could be considered to be in the critical region near the $^5T_2/^1A_1$ crossover for iron(II).[21,22]

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The different magnetic properties of the iron complexes of (1) and (2) call for comment in the light of the virtually identical field strengths observed. It is believed that steric rather than electronic factors are responsible for the different behaviour. Irrespective of the ligand field strength in a high-spin nickel(II) complex, the ligand must be sterically capable of close approach to the metal atom if it is to induce spin-pairing in iron(II), since a change from high-spin to low-spin states will involve a reduction in the radius of Fe^{2+}.[23] The free pyridine ring in (2) is believed to hinder this necessary closer approach to the metal atom and thus the ligand is not able to effect spin-pairing in iron(II).

The reduction in the field strength of terpyridine by replacement of one of the pyridine rings by a five-membered heterocycle can be expected to result more from structural than electronic effects. In consideration of the present series of ligands, however, it is pertinent to recall that thiazole is a weaker base than pyridine[13,24] and thus the electronic and structural effects would be cooperative in reducing the field strength. Although the relationship between these ligands and terpyridine is significant, their similarity to 2,4-bis(2-pyridyl)thiazole is perhaps equally relevant. The latter ligand induces a spin transition in iron(II)[8] and from the unusually large values for the quadrupole splitting in the Mössbauer spectrum of its iron(II) complex a considerable deviation from cubic symmetry can be deduced.[9] Similar distortions can be expected in the complexes of (1)–(4). In addition to the usual effects of spin–orbit coupling, the degeneracy of the $^5T_2$ state will be lifted further by the introduction of low-symmetry components into the ligand field[25] and in this way the energy barrier separating the quintuplet and singlet states may be surmounted more readily.

Experimental

Preparation of the Ligands

2-(1,10-Phenanthrolin-2-yl)thiazole (1)

1,10-Phenanthroline-2-carbothioamide[12] (2·4 g) was dissolved in chloroacetaldehyde (50 ml) and the solution refluxed for 30 min. The excess chloroacetaldehyde was then distilled off under reduced pressure and the tarry residue was dissolved in 5M hydrochloric acid (30 ml). The solution was boiled with charcoal, filtered and cooled in an ice bath. Sufficient concentrated sodium hydroxide solution was then added to cause precipitation of the *product*, which was obtained as a light tan powder, melting at 125° after recrystallization from ethanol (Found: C, 66·7; H, 3·7; N, 15·8. $C_{15}H_9N_3S,0\cdot5H_2O$ requires C, 66·2; H, 3·7; N, 15·5%).

2-(1,10-Phenanthrolin-2-yl)-4-(2-pyridyl)thiazole (2)

A solution of ω-bromoacetylpyridine (2 g) in ether (50 ml) was slowly added to a solution of 1,10-phenanthroline-2-carbothioamide (2·4 g) in hot ethanol (120 ml). The solution was stirred and left to cool. After 24 h fine yellow crystals of the hydrobromide of (2) had separated. These were filtered off and dissolved in hot water (150 ml). The solution was made basic with sodium hydroxide solution and the mixture cooled in an ice bath. The *product* separated as a yellow powder and was obtained as yellow needles after recrystallization from ethanol, m.p. 235° (Found: C, 70·2; H, 3·7; N, 16·4. $C_{20}H_{12}N_4S$ requires C, 70·6; H, 3·6; N, 16·5%).

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2-(1,10-Phenanthrolin-2-yl)thiazolidine (3)

1,10-Phenanthroline-2-carbaldehyde[26] (2·08 g) and 2-aminoethanethiol (0·77 g; excess), each dissolved in the minimum volume of hot ethanol, were mixed. The colour of the solution intensified immediately and after a short time crystals formed. These were collected and redissolved in ethanol. The solution was boiled with decolorizing charcoal and the *product* crystallized on cooling. After a further recrystallization from benzene it was obtained colourless and had m.p. 138–140° (Found: C, 67·5; H, 4·9. $C_{15}H_{13}N_3S$ requires C, 67·4; H, 4·9%).

2-(1,10-Phenanthrolin-2-yl)benzothiazole (4)

To a solution of 1,10-phenanthroline-2-carbaldehyde (1·7 g) in warm ethanol (5 ml) 2-aminobenzenethiol (0·9 g) was added. Almost immediately cream crystals formed. These were very susceptible to oxidation and when exposed to the atmosphere they collapsed and darkened. They were dissolved in hot ethanol (200 ml) and the solution was refluxed, while air was passed through it, for 30 h. After the solution was boiled with decolorizing charcoal its volume was reduced to 50 ml and cream *crystals* separated. After being recrystallized from aqueous ethanol the sample had m.p. 210–212° (Found: C, 72·4; H, 3·6. $C_{19}H_{11}N_3S$ requires C, 72·8; H, 3·5%).

Preparation of the Complexes

$[ML_2][BF_4]_2$ (*L* = (*1*), (*2*), (*3*), (*4*))

These complexes were all prepared by interaction of ethanolic solutions of the ligands and the stoichiometric amount of metal fluoroborate. The products crystallized directly from these solutions and were dried in vacuum at 60°.

$[FeL_2][X_2]$ (*L* = (*2*); *X* = *I*, *Br*, NO_3)

To a solution of (2) (0·68 g) in hot ethanol (50 ml) was added a solution of iron(II) chloride tetrahydrate (0·4 g) in hot ethanol (10 ml). The brown mono-ligand complex $[FeLCl_2]$ immediately crystallized. This was dissolved in hot water, the solution kept near 100° for several minutes and then filtered. When a saturated solution of the appropriate sodium salt was added and the solution cooled the bis-ligand complexes crystallized. They were washed with a little cold water, then ethanol, and dried at 60°.

Physical Data

Solution spectra of the nickel complexes were obtained on a Zeiss PMQ II spectrophotometer.

Magnetic data were collected by means of a Newport variable temperature Gouy balance. Magnetic susceptibilities were corrected for diamagnetism (values of Δ, the diamagnetic correction, are given in Table 2).

Acknowledgments

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