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Coordination of Conjugated Imine Systems with Group VIIIA Metals. I. Iron and Ruthenium Complexes of 2-(2-Pyridyl)thiazole

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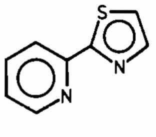
The bidentate 2-(2-pyridyl)thiazole (L) shows a closer similarity to 2,2'-bipyridine than do other pyridine derivatives containing a five-membered heterocyclic substituent. Thus the iron(II) complex is low-spin, at least to 383K, despite a field strength about nickel in $[NiL_3]^{2+}$ *which is in the critical Fe(II) crossover region. The spectroscopic properties of the ruthenium(II) complexes* $[RuL_3]^{2+}$, $[RuL_2bipy]^{2+}$ *and* $[RuL(bipy)_2]^{2+}$ *and of the corresponding ruthenium(III) complexes are very similar to those of* $[Ru(bipy)_3]^{3+/2+}$*, as are the reduction potentials. These similarities are ascribed to the pronounced* π*-acceptor capacity of the thiazole moiety.*

Introduction

The replacement of one of the pyridyl groups in 2,2'-bipyridine or 2,2',2"-terpyridine with a suitable five-membered heterocycle can be achieved readily with retention of the basic di-imine or ter-imine structural fragment but with considerably altered coordinating capacity of the bases. This is manifested most strikingly, in a large number of instances, by the reduction in the field strength to the critical level whereby a singlet–quintet spin transition within the bivalent iron complexes can be induced [1]. In the bidentate series this effect is shown by the replacement of a pyridine ring in bipyridine by, for example, an imidazole [2] and in the tridentate terpyridine series by a thiazole moiety [3].

Thiazole is closely akin to pyridine in its aromaticity and general chemistry [4]. Strong similarities have been noted too in the coordination derivatives of the two bases [5, 6]. When the thiazole system is incorporated into a chelate molecule the differences which emerge must have their origins primarily in structural factors since the five-membered heterocycle will impose a greater 'bite' to the chelate ring and thereby introduce some distortion into the metal ion environment.

The present study of the bidentate 2-(2-pyridyl)-thiazole (I) (abbreviated L in subsequent formulae) has been undertaken principally for two reasons. In the first instance the effect of the incorporation of a thiazole moiety into a di-imine system on the ground-state of iron(II) is examined and, secondly, the influence of the moiety on the properties of the related ruthenium(II) complexes is relevant to the growing interest in ruthenium di-imine complexes, in the light of the remarkable spectroscopic and photochemical properties of the parent species, $[Ru(bipy)_3]^{2+}$ [7].



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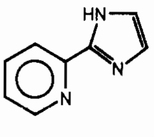

II

Results and Discussion

Coordination with Iron

2-(2-Pyridyl)thiazole has been known for some time, though its complexes have received only very limited attention. Knott and Breckenridge [8] noted the less intense colour of the iron(II) complex of (I), compared to that of $[Fe(bipy)_3]^{2+}$. Later quantitative work by Eilbeck and co-workers [9] revealed a much lower overall formation constant for $[FeL_3]^{2+}$ and a sequence of stepwise formation constants significantly different from those for the bipyridine complex. For the latter complex the third stepwise formation constant is the greatest and this is associated with a change from a high-spin $t_{2g}^4 e_g^2$ to a low-spin $t_{2g}^6 e_g^0$ electronic configuration for the metal atom on coordination of the third ligand molecule. It thus seemed desirable to confirm the spin-state of iron in $[FeL_3]^{2+}$, particularly in the light of the effect of several related ligands containing five-membered heterocycles in inducing a spin transition in iron(II).

The likely spin-state of iron in its complexes can be predicted with some certainty from the estimate of 10 Dq obtained from the position of ν_1 (the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition) in the spectrum of the correspond-

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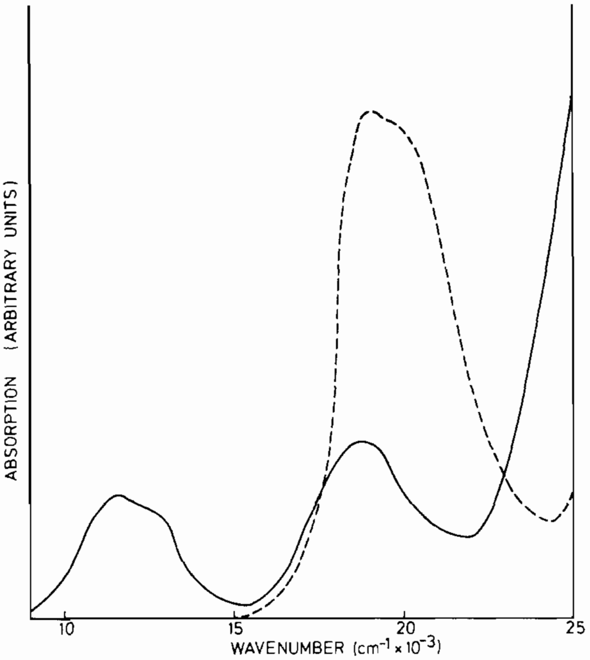

Fig. 1. Absorption spectrum of $[NiL_3][BF_4]_2$ (——) and $[FeL_3][BF_4]_2$ (– – –) in nitromethane solution.

ing nickel complex [10]. For $[NiL_3]^{2+}$ this transition is observed as a broad, unsymmetrical band with a maximum at 11600 cm^{-1} (Fig. 1). The shoulder on the high energy side of this band is assigned to the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition in accord with assignments to the spectrum of $[Ni(bipy)_3]^{2+}$ [11]. Robinson, Curry and Busch [10] noted that this lower intensity component of the ν_1 band of the spectra of a series of related nickel complexes appeared to approach ν_1 from the high-energy side and move to lower energies as 10 Dq increased. In the spectrum of $[Ni(bipy)_3]^{2+}$ it appears on the low-energy side of ν_1 and, consistent with this, in this complex 10 Dq (12650 cm^{-1}) is significantly greater than in $[NiL_3]^{2+}$ (11600 cm^{-1}). The $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition (ν_2) occurs as a symmetrical band centered at 18700 cm^{-1} leading to a ratio of ν_2/ν_1 of 1.63, which is compatible with essentially octahedral coordination of the metal atom [12]. The actual value for 10 Dq (Ni^{2+}) in $[NiL_3]^{2+}$ is in the critical range within which the spin-state of the corresponding iron(II) complex can be expected to vary and is only marginally greater than that for $[Ni(pyim)_3]^{2+}$ (pyim = 2-(2-pyridyl)imidazole (II)) (11500 cm^{-1}; measured in the present work for a solution of the complex in nitromethane – the previously quoted value, 11070 cm^{-1} was obtained for a solid sample [13]). $[Fe(pyim)_3]^{2+}$ displays a spin-state transition [2].

TABLE I. Magnetic Data for $[FeL_3][BF_4]_2$.

T	$10^6 \times \chi'_M$ (cm^3 mol^{-1})	μ (B.M.)
303	400	0.98
323	400	1.01
343	410	1.05
363	430	1.11
383	440	1.16

The intensely violet complex $[FeL_3][BF_4]_2$ was readily obtained by interaction of the ligand with iron(II) fluoroborate in ethanol. In the solid state at room temperature the complex is essentially diamagnetic (Table I), the slight paramagnetism observed being more or less normal for iron in the $^1A_{1g}$ state and arising from mixing in of higher states via spin–orbit coupling [14]. The possibility that a temperature-induced spin transition occurs at elevated temperatures does not seem likely from the data obtained (Table I), at least to 383 K. The slight temperature dependence observed for the magnetic moment is not considered significant in this respect.

The replacement of a pyridine ring in bipyridine by a thiazole obviously has, then, a rather different effect to replacement by an imidazole ring which is structurally, but not electronically, similar to a thiazole. The imidazole derivative is the stronger base but the π-acceptor capacity of the thiazole is expected to be greater because of the accessibility of vacant *d* orbitals on the sulfur atom [9, 13]. This would be expected to result in a stabilisation of the low-spin state for iron in $[FeL_3]^{2+}$. Nevertheless, the purely low-spin nature of $[FeL_3][BF_4]_2$ appears somewhat surprising in view of the relatively low formation constant observed for the complex cation. Solution studies of its magnetism are not meaningful since the complex breaks down appreciably, virtually instantaneously and completely in dimethylformamide but quite slowly in acetone. The electronic spectrum measured by Knott and Breckenridge (presumably for an aqueous solution) shows the typical $t_2 \rightarrow \pi^*$ charge-transfer transition associated with the low-spin iron(II) di-imine chromophore [8]. The intensity of this band (ϵ = 6500 mol^{-1} cm^2) was found to be only about one half of that of the corresponding band in the spectrum of $[Fe(bipy)_3]^{2+}$. We have observed essentially the same spectrum in acetone solution (Fig. 1) but noted that the intensity diminished as the solution aged. The relatively low value for ϵ could therefore be due to decomposition. The spectrum does indicate, however, the presence of a low-spin species in solution.

Coordination with Ruthenium

The current interest in the unusual photoactive properties of $[Ru(bipy)_3]^{2+}$ has led to the study of

TABLE II. Electronic Spectral Data, Band Maxima (cm^{-1}).

Complex	Charge Transfer Bands	
	Absorption	Emission
$[RuL_3]^{2+}$	21600	16950
$[RuL_2bipy]^{2+}$	21830	16750
$[RuL(bipy)_2]^{2+}$	22080	16720
$[RuL_3]^{3+}$	12900	
$[RuL_2bipy]^{3+}$	13350	
$[RuL(bipy)_2]^{3+}$	14100	

TABLE III. Reduction Potentials in 1 *M* HNO_3 Solution.

System	E (v)
$[RuL_3]^{3+/2+}$	1.28
$[RuL_2(bipy)]^{3+/2+}$	1.27
$[RuL(bipy)_2]^{3+/2+}$	1.26

a number of related systems in which the ligand has been modified structurally [15–17]. Although these modifications have included the incorporation of five-membered heterocycles [1, 8], thiazole derivatives have not been described. The close similarity noted above in the iron(II) complexes of (I) and those of bipyridine suggests that strong similarities in the ruthenium complexes of the two bases may also be evident.

The three complexes $[RuL_3]^{2+}$, $[RuL_2bipy]^{2+}$ and $[RuL(bipy)_2]^{2+}$ were prepared so as to examine the effect of successive replacement of bipyridine. Slow decomposition of the complexes in solution was evident only after prolonged standing in acid. The complex perchlorates are all diamagnetic. Considerable effort has been devoted to detection and separation of the possible geometrical isomers of $[RuL_3]^{2+}$ and $[RuL_2bipy]^{2+}$, arising from the unsymmetrical nature of (I). Fractional crystallisation, paper and column chromatographic techniques failed to separate any products identifiable as isomers.

The electronic spectral characteristics of all three complexes are very similar to those of $[Ru(bipy)_3]^{2+}$ (Table II) [19]. The spectrum of $[RuL_3]^{2+}$ shown in Fig. 2 is typical. The principal charge-transfer transition occurs at about 22000 cm^{-1} ($\epsilon \sim 13500$ mol^{-1} cm^2) and appears as an unsymmetrical band with a shoulder on the high-energy side. Additionally, as in the bipyridine series, there is a marked similarity in the shape of this band in the spectra of $[RuL_3]^{2+}$ and $[FeL_3]^{2+}$. The shoulder presumably has its origins in a vibrational progression, as has been indicated for the bipyridine systems [20]. The successive decrease of the $t_2 \rightarrow \pi^*$ transition to lower energies as the number of coordinated thiazole molecules increases is probably associated with a slightly greater π-acceptor capacity of the thiazole ring. The intense intra-ligand transition observed at 33200 cm^{-1} in the spectrum of the free ligand [8] remains undisplaced in the spectra of the complexes.

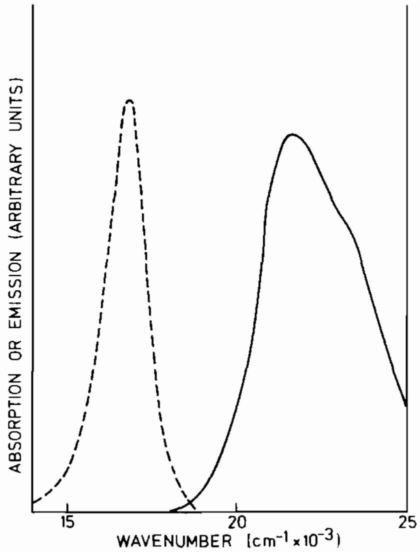

Fig. 2. Absorption spectrum (——) and emission spectrum (– – –) of $[RuL_3]^{2+}$ in ethanol and water, respectively.

The trivalent complexes $[RuL_3]^{3+}$, $[RuL_2bipy]^{3+}$ and $[RuL(bipy)_2]^{3+}$ were prepared *in solution only* by oxidation of the corresponding bivalent complexes with cerium(IV) nitrate in nitric acid. They are all green and their visible spectra show a band of moderate intensity ($\epsilon \sim 500$ mol^{-1} cm^2) which is assigned to a metal reduction charge-transfer transition. In all instances this band is observed at lower energies than for $[Ru(bipy)_3]^{3+}$ [21] and the shift to lower energies increases as the number of coordinated thiazole molecules increases (Table II). Again this is consistent with trends observed in the spectra of the bivalent complexes and is indicative of the increased stabilisation of ruthenium(II) by the greater π-acceptor nature of thiazole. This is reflected, too, in the values for the Ru(III)/Ru(II) reduction potentials listed in Table III. Although there is little difference in the actual values there is a slight but real shift to higher potentials with increased coordination of thiazole.

The Ru(III) species were not isolated and in acidic solution they slowly revert to the corresponding Ru(II) complexes. This redox behaviour is reversible over a large number of cycles.

The three Ru(II) complexes are luminescent and, as in the absorption spectra, there is a close similarity in the emission spectra (Table II and Fig. 2) of these complexes and that of $[Ru(bipy)_3]^{2+}$ [22]. Excitation maxima for all complexes were observed at *ca.* 475 nm. The overall spectral characteristics of these thiazole derivatives thus closely parallel those of the $[Ru(bipy)_3]^{2+}$ ion and suggest that their photochemistry may well be equally as rich as that of the bipyridine complex. Further studies on these aspects are presently being undertaken.

Comparison of the properties of (I), as shown in the present study, with those of (II) reveals the importance of the greater π-acceptor nature of (I). Despite its weaker basicity, this capacity enables (I) to effect complete spin-pairing in iron(II). The close similarities in the spectral and redox properties of the ruthenium complexes of (II) and bipyridine also can be ascribed to the importance of π-bonding contributions. The complexes of (II) with ruthenium are also similar to those of bipyridine but not to the same extent [23] and the important differences which are observed (a hypsochromic shift of the main Ru(II) charge-transfer transition and a movement of E (Ru(III)/Ru(II)) to more negative values) can be correlated with the reduced π-acceptor capacity of (II).

Experimental

2-(2-Pyridyl)thiazole (I)

The ligand (I) was prepared from picolinic acid thioamide and bromoacetal as described by Glover and Thomas [24]. M.P. 62–61.5° (Lit. [24] 59–61°) (Found %: C, 59.0; H, 3.5; N, 17.1. $C_8H_6N_2S$ requires: C, 59.2; H, 3.7; N, 17.3).

Tris[2-(2-pyridyl)thiazole]iron(II) fluoroborate

A hot, filtered solution of iron(II) fluoroborate hexahydrate (0.34 g, 1 mmol) in ethanol (15 ml) was added with stirring to a hot solution of (I) (0.49 g, 3 mmol) in ethanol (15 ml) under an atmosphere of nitrogen. An intensely red-violet solution was obtained and deep purple-red crystals separated. These were washed with ethanol and dried *in vacuo* (Found %: C, 40.9; H, 2.5; N, 12.2; Fe, 7.6. $C_{24}H_{18}N_6S_3FeB_2F_8$ requires C, 40.3; H, 2.5; N, 11.7; Fe, 7.8).

Tris[2-(2-pyridyl)thiazole]nickel(II) Fluoroborate Dihydrate

A hot, filtered solution of nickel(II) fluoroborate hexahydrate (0.34 g, 1 mmol) in ethanol (10 ml) was added to a hot solution of (I) (0.49 g, 3 mmol) in ethanol (10 ml). Ether (20 ml) was carefully added to the pale violet solution when lilac crystals of the product deposited. These were washed with a little ethanol/ether and dried *in vacuo* (Found %: C, 37.9; H, 2.9; N, 11.1; Ni, 7.7. $C_{24}H_{18}N_6S_3NiB_2F_8 \cdot 2H_2O$ requires: C, 38.2; H, 2.9; N, 11.1; Ni, 7.8).

Tris[2-(2-pyridyl)thiazole]ruthenium(II) Perchlorate and Iodide Dihydrate

The following procedure utilises glycerol both as reaction medium and reducing agent, a preparative method described initially by Dwyer and Gyarfas [25] for the preparation of $[Os(phen)_3]^{2+}$ and applied later by others to ruthenium syntheses [26]. A mixture of $K_4[Ru_2Cl_{10}O] \cdot H_2O$ [27] (0.45 g, 0.0012 mol) and 2-(2-pyridyl)thiazole (0.58 g, 0.0036 mol) in glycerol (8 ml) was placed in a test tube and heated carefully over a bunsen burner until a clear, deep orange-red solution was obtained. This was cooled and water (20 ml) was added. The solution was filtered to remove traces of ruthenium metal and to the filtrate a concentrated aqueous solution of either sodium perchlorate or sodium iodide was added. The products crystallised immediately. They were washed with a little ice-cold water, recrystallised from hot water and dried *in vacuo.* (Found %: C, 36.7; H, 2.2; N, 10.5; Ru 12.6. $C_{24}H_{18}N_6S_3RuCl_2O_8$ requires: C, 36.7; H, 2.3; N, 10.7; Ru, 12.9. Found %: C, 32.8; H, 2.6; N, 9.4; Ru, 11.3. $C_{24}H_{18}N_6S_3RuI_2 \cdot 2H_2O$ requires: C, 32.9; H, 2.5; N, 9.6; Ru, 11.5).

Bis[2-(2-pyridyl)thiazole]-2,2'-bipyridine Ruthenium(II) Perchlorate and Iodide Tetrahydrate

A mixture of (I) (0.55 g, 3.4 mmol) and $NH_4[RuCl_4bipy]$ [28] (0.71 g, 1.7 mmol) in 1:1 ethanol/water (40 ml) was refluxed for two hours on the water bath. The solution was then evaporated to 15 ml, filtered and either sodium iodide or sodium perchlorate solution added to the filtrate. The bright orange products separated, were washed with a little cold water and recrystallised from hot water. They were dried *in vacuo* (Found %:C, 40.0; H, 2.2; N, 10.5; Ru, 13.2. $C_{26}H_{20}N_6S_2RuCl_2O_8$ requires: C, 40.0; H, 2.6; N, 10.8; Ru, 13.0. Found % C, 34.8; H, 3.6; N, 9.0; Ru, 11.0; $C_{26}H_{20}N_6S_2RuI_2 \cdot 4H_2O$ requires: C, 34.4; H, 3.1; N, 9.3; Ru, 11.1).

2-(2-Pyridyl)thiazole-bis(2,2'-bipyridine)ruthenium(II) Perchlorate Dihydrate and Iodide Tetrahydrate

To a warm solution of *cis*$[Ru(bipy)_2Cl_2]$ [29] (0.5 g, 1 mmol) in methanol (10 ml) and water (10 ml) was added (I) (0.18 g, 1.1 mmol). The mixture was refluxed on the water bath for two hours then evaporated to dryness. The residue was dissolved in 0.1 *M* hydrochloric acid (10 ml) to give a clear red-orange solution. This solution was warmed and then either sodium perchlorate or sodium iodide solution was added whereupon the products crystallised. They were washed with a little ice-cold water, recrystallised from hot water and dried *in vacuo.* (Found %: C, 41.8; H, 3.4; N, 10.6; Ru, 12.2. $C_{28}H_{22}N_6SRuCl_2O_8 \cdot 2H_2O$ requires: C, 41.5; H, 3.2; N, 10.4; Ru, 12.5. Found %: C, 37.0; H, 3.7; N, 8.9; Ru, 11.2; $C_{28}H_{22}N_6SRuI_2 \cdot 4H_2O$ requires: C, 37.3; H, 3.4; N, 9.3; Ru, 11.2).

Magnetic Measurements

Magnetic data were obtained using a variable temperature Newport Gouy balance, calibrated with mercury cobalt thiocyanate.

Spectral Measurements

Absorption spectra were measured with a Zeiss PMQII spectrophotometer. Spectral data for $[NiL_3][BF_4]_2$ and $[Ni(pyim)_3][BF_4]_2$ were obtained for solutions in nitromethane; for $[FeL_3][BF_4]_2$ in acetone solution; for the Ru(II) complexes in ethanol and for the Ru(III) complexes in 1 *M* nitric acid. Emission spectra were obtained for aqueous solutions at room temperature with an Hitachi Perkin Elmer MPF-2A fluorescence spectrophotometer equipped with a xenon lamp.

Redox Measurements

Reduction potentials were determined by potentiometric titration of solutions of the Ru(II) complexes in 1 *M* HNO_3 with cerium(IV) ammonium nitrate also in 1 *M* HNO_3, using a smooth platinum electrode in conjunction with a saturated calomel electrode. The potentials given in Table III refer to the hydrogen electrode as standard. In all titrations the end-point corresponded to a one-electron change. The $[Ru(bipy)_3]^{3+/2+}$ system was found to have a potential of 1.259 v (lit. [30] 1.257 v) under the experimental conditions used in the present work.

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