Synthesis, Reactions and Copper(II), Nickel(II), and Zinc(II) Complexes of *N*-(2-Pyridinyl)ketothioacetamides†

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The synthesis and properties of two *N*-(2-pyridinyl)ketothioacetamide ligands, HL [(**4**)], and their complexes with nickel(II), copper(II), and zinc(II) are described. The ligands are potential O,S,N donors and are sulphur analogues of the O,O,N donor *N*-(2-pyridinyl)ketoacetamide ligands (**1**). The failure of certain thionation methods in the preparation of (**4**) from (**1**) is demonstrated. Ligands (**4**) show analogous spectroscopic properties to those of (**1**) and display thioketo–enol tautomerism in solution but readily oxidize to the 2*H*-pyrido[2,3-*a*][1,2,4]thiadiazoles (**5**). This redox activity is shown to be decreased at low temperatures and eliminated in the *N*-benzyl-*N*-(2-pyridinyl)ketothioacetamides (**6**), the *N*-benzylated derivatives of (**4**). Complexes of the type [ML_2] (M = Ni^{II}, Cu^{II} or Zn^{II}) display spectral and magnetic properties typical of four-co-ordinate complexes in which co-ordination of the ligands is *via* the S,N donor sets with the O donor remaining unco-ordinated. E.s.r. spectra of a [CuL_2] complex doped into [NiL_2] and [ZnL_2] lattices show marked differences depending on the host, with the former being typical of planar co-ordination while the latter gives a rather unusual lineshape of distorted tetrahedral geometry.

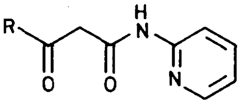
We have recently reported on the binucleating ability of the *N*-(2-pyridinyl)ketoacetamide ligands (**1**) with copper(II) which give binuclear complexes showing very strong antiferromagnetic coupling.[1] These ligands contain O,O,N donor atoms and co-ordinate to give an essentially coplanar *trans*-[Cu_2L_2]$^{2+}$ unit in the complexes, with the amido oxygen atoms bridging the two metal ions.

In the present paper we describe the synthesis of the *N*-(2-pyridinyl)ketothioacetamide ligands (**4**) (HL), the thioamide analogues of (**1**). These ligands contain O,S,N donor atoms with the prospect of showing similar co-ordination properties to (**1**).

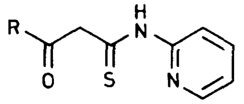
Few examples of potentially S-bridging binucleating ligands are known[2,3] and little is known of the co-ordination chemistry and magnetostructural features around the sulphur atom in binuclear complexes of such ligands.[4,5] Part of the reason for this scarcity is the difficulty encountered in ligand synthesis because of the tendency of the sulphur atom to form stable heterocyclic species.[6,7] Moreover, a formidable and rarely fully investigated problem is ligand oxidation, often assisted by redox-active metal ions.[3] We also describe here our experiences with the reactivity of (**4**), which is prone to both types of side reaction, and describe a series of mononuclear complexes of type [ML_2], where M = Ni^{II}, Cu^{II}, or Zn^{II}. It has not been possible to prepare binuclear metal complexes of the ligands (**4**). We believe this to be due to steric inflexibility of the ligand and hence inability to allow a pyramidal bridging S atom, which would be required in such complexes.

Results and Discussion

Attempted Synthesis of (**4**) *by Thionation of* (**1**).—The *N*-(2-pyridinyl)ketoacetamides (**1**) can be viewed either as keto-substituted *N*-(2-pyridinyl)acetamides or as 2-pyridinylamino-substituted β-diketones. Since the pyridinylacetamide and β-diketone fragments are separately known to undergo thionation reactions[8–10] it seemed likely that at least one of the oxygen atoms in (**1**) could be replaced by sulphur. It was not obvious at the outset which of the oxygen atoms would be preferentially substituted although it was felt that if the amido function predominated, the desired thioamides (**4**) would be favoured.



(**1**)



(**4**)

R = Me (**a**) or Ph (**b**)

The compound P_4S_{10} has been used successfully to convert pyridinylamides, such as *N*-(2-pyridinyl)benzamide, into the corresponding thioamides.[11,12] We found that thionation of (**1**) using P_4S_{10} in pyridine did not yield (**4**) but rather the stable heterocyclic species (**2**) (see Scheme). The cyclization is apparently effected through nucleophilic attack on the keto moiety by the pyridine nitrogen of the amido moiety with subsequent loss of water. It is uncertain whether thionation precedes cyclization or *vice versa*. Variation of ratios of reactants, reaction conditions, and solvents did not lead to the formation of other products. Cyclization reactions of this type have been reported previously[6,7] and a number of related heterocycles have been obtained by a similar route.[13]

The thionation of β-diketones $RCOCH_2COR'$ (R,R′ = alkyl or aryl) has most commonly involved the use of H_2S and HCl to produce only one of the two possible monothio-β-diketone isomers depending on the relative electron-withdrawing power of the R and R′ substitutents.[9,10] It was not evident to us which isomer would be favoured in the case of (**1**), since to our knowledge no monothio-β-diketones with an R = amine substituent have been prepared *via* this method. Treatment of a H_2S-saturated ethanolic solution of (**1b**) with gaseous HCl yielded the isomer (**3**) and not the desired (**4b**). Compound (**3**) was found to hydrolyze to the hydrated hydrochloride of (**1b**) in warm 95% ethanol with the evolution of H_2S. The crystal structure of the hydrated hydrochloride product of (**1b**) has been reported separately.[1] Under identical reaction conditions (**1a**) was found not to react with H_2S.

Synthesis of Ligands HL^1 [(**4a**)] *and* HL^2 [(**4b**)].—The successful synthesis of (**4**) was based on a modification of the Worrall method[14] using 'one-pot' reaction conditions. The sodium salts of the appropriate β-diketone, acetylacetone and dibenzoylmethane respectively [Na(RCOCHCOR)], were

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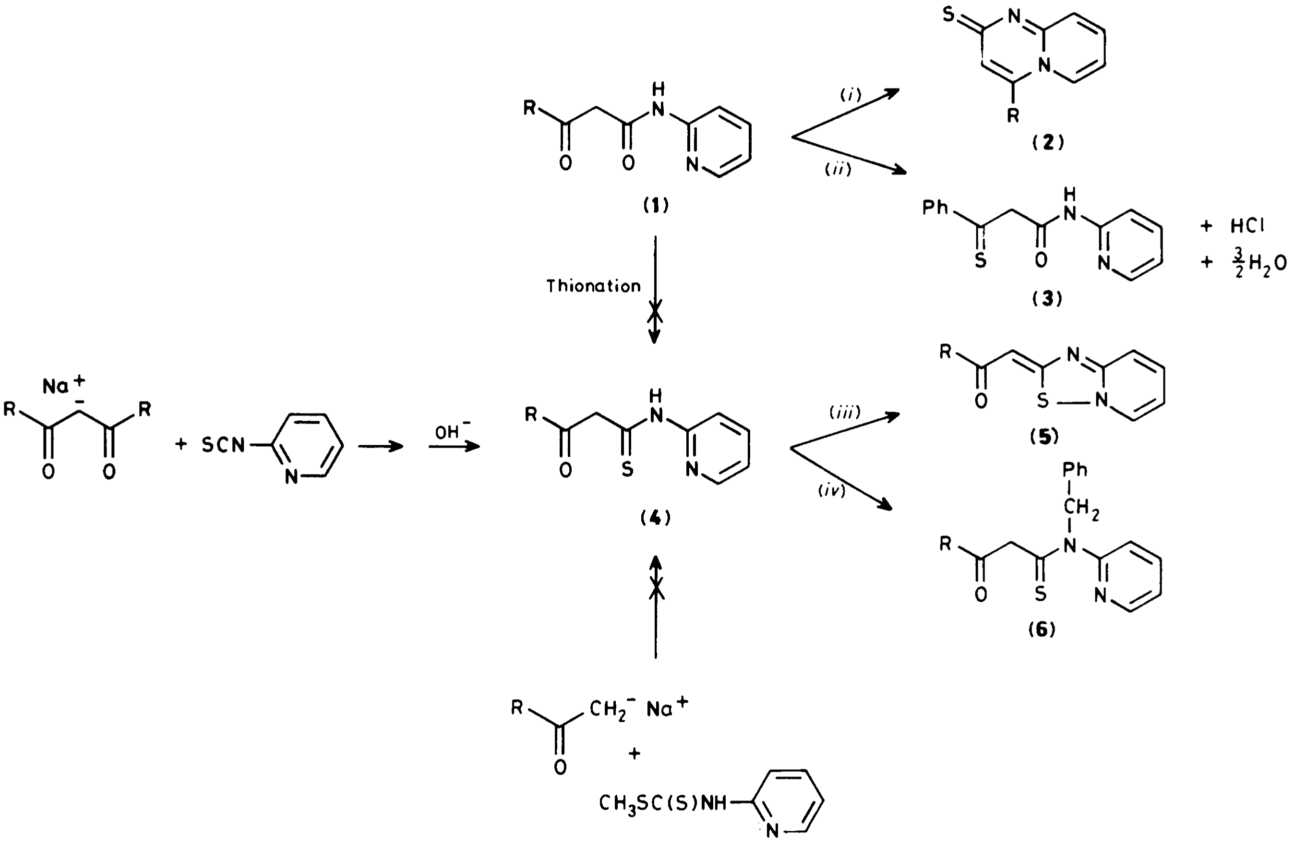
† *Non-S.I. unit employed:* B.M. = 9.274×10^{-24} J T^{-1}.



Scheme. (*i*) P_4S_{10}, pyridine; (*ii*) R = Ph, H_2S, HCl; (*iii*) $K_3[Fe(CN)_6]$, OH^-; and (*iv*) $PhCH_2Cl$, OH^-

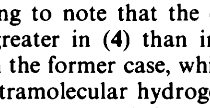
treated with 2-isothiocyanatopyridine* to yield the salts of the thioanilide intermediates. The intermediate salts were dissolved *in situ* by the addition of dilute base to hydrolyze one of the ketonic groups. Neutralization of the basic solution produced yellow crystalline flakes of (**4a**) and (**4b**) respectively.

We found the attempted Claisen condensation[17,18] of ketonic salts $[Na(CH_2OCR)]$ with the appropriate dithioester $[CH_3S–C(S)NHR']$ unsuccessful as an alternative route to (4). While the method has been used in the synthesis of a number of alkyl-substituted monothio-β-diketones, the required ester, *S*-methyl *N*-(2-pyridinyl)dithiocarbamate,[19] appears to be less susceptible to nucleophilic attack by the ketonic anion than does the isothiocyanate in the Worrall method. The reason for this is probably that the carbon in the dithio ester group is less electrophilic (due to the electron-donating amine substituent) than in the alkyl substituted esters and hence will not readily undergo a nucleophilic attack.

The spectral properties of (4) show similarities to those of the amido analogues (1) already reported.[1] The i.r. spectra of (**4a**) and (**4b**) each show two ν(NH) bands [3 180, 3 130 cm^{-1} and 3 200, 3 120 cm^{-1} respectively] (Table 1). The ν(CO) bands in the i.r. spectrum of (**4a**) at 1 720 and 1 615 cm^{-1} show contributions from both thioketo and enol tautomers, whereas for (**4b**) a greater contribution from the enol tautomer is evident from the band at 1610 cm^{-1}. We have been unable unambiguously to assign ν(CS) bands from the complicated nature of the spectra.

Evidence of thioketo–enol tautomerism is provided by the proton and ^{13}C n.m.r. spectra of (**4**) in chloroform solution (Figure 1). The behaviour in solution follows similar patterns to those observed for (**1**).[1] The n.m.r. studies show a larger thioketo contribution (59%) in (**4a**) than in (**4b**) (33%). In both cases the enol proton in the enol form is largely deshielded *via* hydrogen bonding to the thioamide group [14.5 p.p.m. in (**4a**) and 14.9 p.p.m. in (**4b**)]. From the n.m.r. spectra, the molecular conformation of (4) in solution appears to follow the behaviour observed[11,20] for compounds containing the *N*-(2-pyridinyl)-thioamide moiety, by which H^3 is brought near the thiocarbonyl group and experiences an anisotropic deshielding effect.

It is also interesting to note that the deshielding effect on the NH proton is greater in (**4**) than in (**1**) because of the higher NH acidity in the former case, which is directly related to the strength of intramolecular hydrogen bonding with, for example, the ketonic group (see below). This trend has been reported in the n.m.r. studies of the keto–enol tautomerism of acylthioacetamides when compared to the analogous acetylacetamides.[21]



Various other authors have briefly discussed tautomerism in solution for monothio-β-diketones involving the thioketo, enol, and thioenol tautomers.[9,22,23] The thioenol tautomeric form is less common and there is no spectroscopic evidence for its presence in (4), in either the solid state or in chloroform solution.

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* The synthesis of 2-isothiocyanatopyridine was based on the known[15] pyrolytic reaction of dithiocarbamates RSC(S)NHR' to RSH and R'NCS (R = alkyl, R' = aryl). The synthetic details were kindly provided by J. Reid.[16]

Table 1. Analytical, physical, and spectroscopic data for (**2a**)—(**6b**)

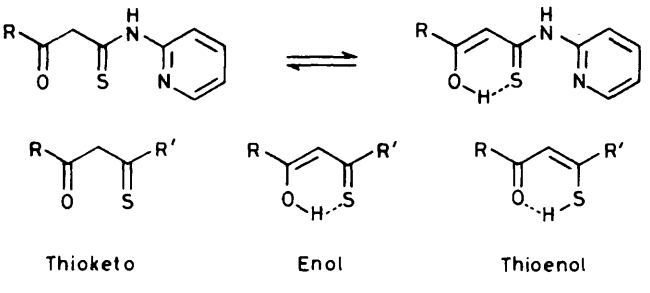
Compound	Appearance	M.p./°C	Analysis[a] (%)				I.r.(cm^{-1})
			C	H	N	S	
(**2a**)	Yellow-orange	278—280	61.6	4.40	15.60	18.4	aromatic 1 620s(br), 1 520m
$C_9H_8N_2S$	flaky needles		(61.3)	(4.60)	(15.90)	(18.2)	
(**3**)[b]	Lemon-yellow	162—163	53.0	5.60	8.65	9.5	ν(CO) 1 650s, 1 630m, ν(NH) 3 320m(br), ν(H_2O)
$C_{14}H_{12}N_2OS{\cdot}HCl{\cdot}1.5H_2O$	microneedles		(52.6)	(5.05)	(8.75)	(10.0)	3 440m(br)
(**4a**)	Pale yellow	83.5—84	55.2	5.40	14.50	16.6	ν(CO) 1 720m, 1 615s, ν(NH) 3 180m, 3 130m, aromatic
$C_9H_{10}N_2OS$	powder		(55.3)	(5.20)	(14.40)	(16.5)	1 595m, 1 575s
(**4b**)	Bright yellow	91—92	65.5	4.60	10.95	12.0	ν(CO) 1 610m(sh), aromatic 1 600m(sh), 1 580s(br),
$C_{14}H_{12}N_2OS$	powder		(65.6)	(4.70)	(10.95)	(12.5)	1 540s(br), ν(NH) 3 200m, 3 120m
(**5a**)	Brown powder	115	55.6	4.55	14.10		ν(CO) 1 625s, aromatic 1 600w(sh), 1 530s(br)
$C_9H_8N_2OS$			(56.2)	(4.20)	(14.55)		
(**5b**)	Bright yellow	228—229	66.4	4.00	11.10		ν(CO) 1 620m, aromatic 1 590w(sh), 1 530s
$C_{14}H_{10}N_2OS$	flaky needles		(66.1)	(3.95)	(11.00)		
(**6a**)	Shiny off-white	172—173	67.3	5.70	9.65		ν(CO) 1 615s, aromatic 1 595s, 1 585s, 1 555s
$C_{16}H_{16}N_2OS$	flakes		(67.6)	(5.65)	(9.85)		
(**6b**)	Pale yellow	162—163	72.5	5.10	8.15		ν(CO) 1 615s, aromatic 1 590s, 1 565s(sh), 1 555s(br)
$C_{21}H_{18}N_2OS$	powder		(72.8)	(5.25)	(8.10)		

[a] Calculated values in parentheses. [b] Cl analysis, 11.3 (11.1%).

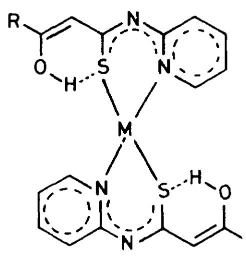
Table 2. Analytical, physical, and spectroscopic properties of [ML_2] complexes {HL = HL^1 [(**4a**)] and HL^2 [(**4b**)]}

Complex	Appearance	M.p.(°C)	Analysis[a] (%)			I.r. (cm^{-1})
			C	H	N	
[NiL^1_2]	Dark brown	230[b]	48.9	4.15	12.55	ν(CO) 1 615s
	microcrystals		(48.6)	(4.10)	(12.60)	
[NiL^2_2]	Dark brown	225[b]	59.3	4.00	9.50	ν(CO) 1 620s
	microcrystals		(59.1)	(3.90)	(9.85)	
[CuL^1_2][c]	Dark brown	150[b,d]	47.9	4.30	11.60	ν(CO) 1 615s
	powder		(48.0)	(4.05)	(12.45)	
[CuL^2_2][e]	Dark brown	190—191[f]	58.9	3.85	10.00	ν(CO) 1 620s
	powder		(58.6)	(3.85)	(9.75)	
[ZnL^1_2]	Yellow flakes	202—204	47.4	3.90	12.75	ν(CO) 1 625s
			(47.8)	(4.00)	(12.40)	
[ZnL^2_2]	Yellow flakes	238—239	58.1	3.85	9.45	ν(CO) 1 630s
			(58.4)	(3.85)	(9.75)	

[a] Calculated values in parentheses. [b] Decomposes. [c] $\mu_{eff.}$(295 K) = 1.74. [d] Colour changes to brown-red at *ca.* 125 °C. [e] $\mu_{eff.}$(295 K) = 1.85. [f] Colour changes to bright orange at 125—126 °C.



Synthesis and Properties of Complexes [ML^1_2] *and* [ML^2_2], (M = Ni^{II}, Cu^{II}, *or* Zn^{II}).—Neutral bis-ligand complexes of (**4**) with nickel(II) and zinc(II) were readily obtained when warm ethanolic solutions of the ligands were mixed with the appropriate metal acetate in ethanol in a 2:1 molar ratio yielding brown microcrystals and yellow microcrystalline flakes, respectively. The spectroscopic data for these complexes (Table 2) indicate that only the S,N donor sets of the ligands are involved in co-ordination.



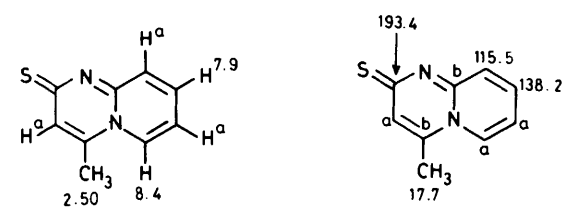
[ML_2], M = Ni^{II}, Cu^{II}, or Zn^{II}

The i.r. spectra of these complexes show the absence of ν(NH) bands and show relatively unchanged ν(CO) bands when compared with the spectra of (**4**). The ketonic ν(CO) band at 1 720 cm^{-1} in (**4a**) is absent in the corresponding complexes due to the predominance of the enol form over the thioketone tautomer in the solid state. The complexes are diamagnetic indicating planar stereochemistry for the nickel(II) complexes.

The ^1H n.m.r. spectra of the complexes (Figure 2) show the presence of the largely deshielded proton of the enol group, which is unco-ordinated, as well as shielded aromatic pyridine protons due to the co-ordination of the metal to the pyridine nitrogen. The deshielding effect on pyridinyl H^3 by the thiocarbonyl group in the free ligands is eliminated on co-ordination of the ligands as rotation of the pyridine group is hindered. This effect of pyridine ring co-ordination has been reported previously.[11] The ^{13}C n.m.r. spectra of chloroform solutions of the complexes also suggest co-ordination of the pyridinyl nitrogen and indicate that the thiocarbonyl group retains most of its double bond character within the six-membered chelate ring leading to comparable CS carbon resonances with those of the corresponding ligands.

Reactions of (**4**) with copper(II) acetate under identical reaction conditions lead to the formation of diamagnetic bright yellow-orange compounds with non-reproducible molecular formulae. The spectral properties of these products and of those formed with other copper(II) salts indicate that oxidation of the ligand had occurred (see below). In order to overcome these adverse reactions, we have developed low-temperature reaction conditions which have allowed the isolation of [$Cu^{II}L_2$] species. These copper(II) complexes were prepared in acetone at low

^{1}H N.m.r | ^{13}C N.m.r. | ^{1}H N.m.r. | ^{13}C N.m.r.

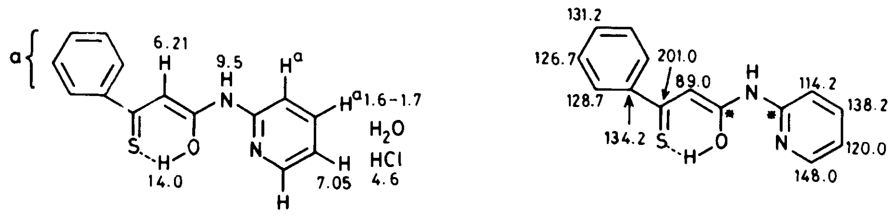


a = 7.1 - 7.5

a = 124·1, 126.7, 131.1

b = 139.9, 147.4

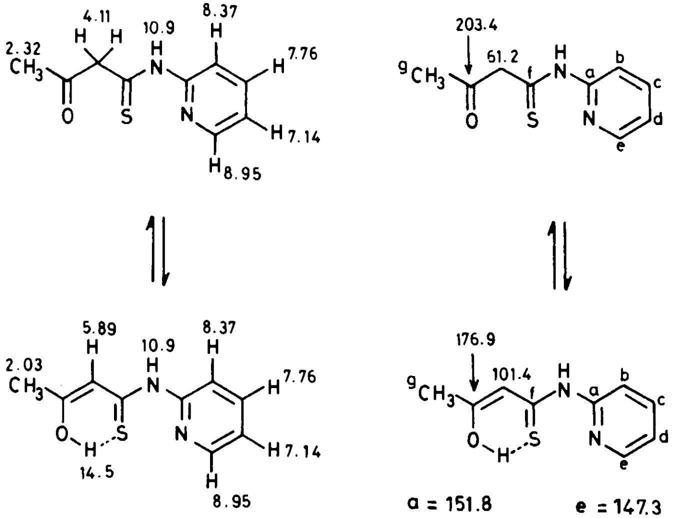
(2a)



a = 7.4 - 8.3

* unobserved

(3)



a = 151.8

b = 118.3, 118.7

c = 138.3

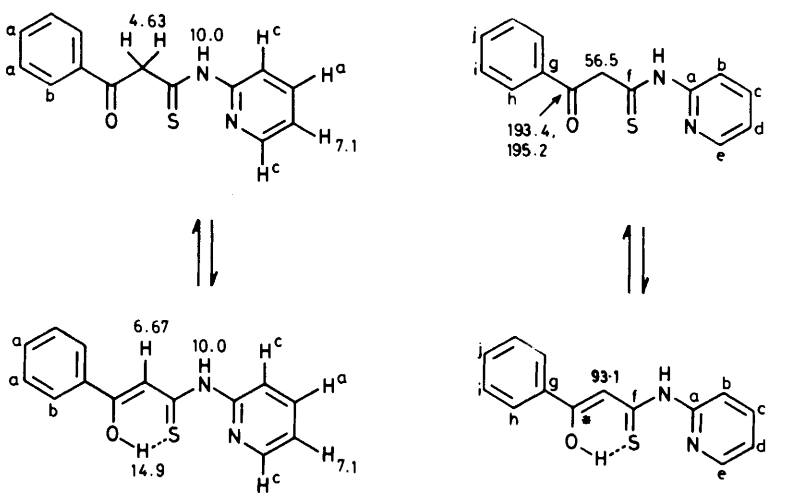
d = 120.6, 121.7

e = 147.3

f = 193.5

g = 23.9, 30.7

(4a)



a = 7.4 - 7.6

b = 7.7 - 7.9

c = 8.3 - 9.1

a = 152.0

b = 115.9, 116.6

c = 138.5

d = 120.6, 121.6

e = 148.2

f = 185.7

g = 134.9, 135.9

h = 128.7

i = 126.9, 127.1

j = 131.3, 132.3

* unobserved

(4b)

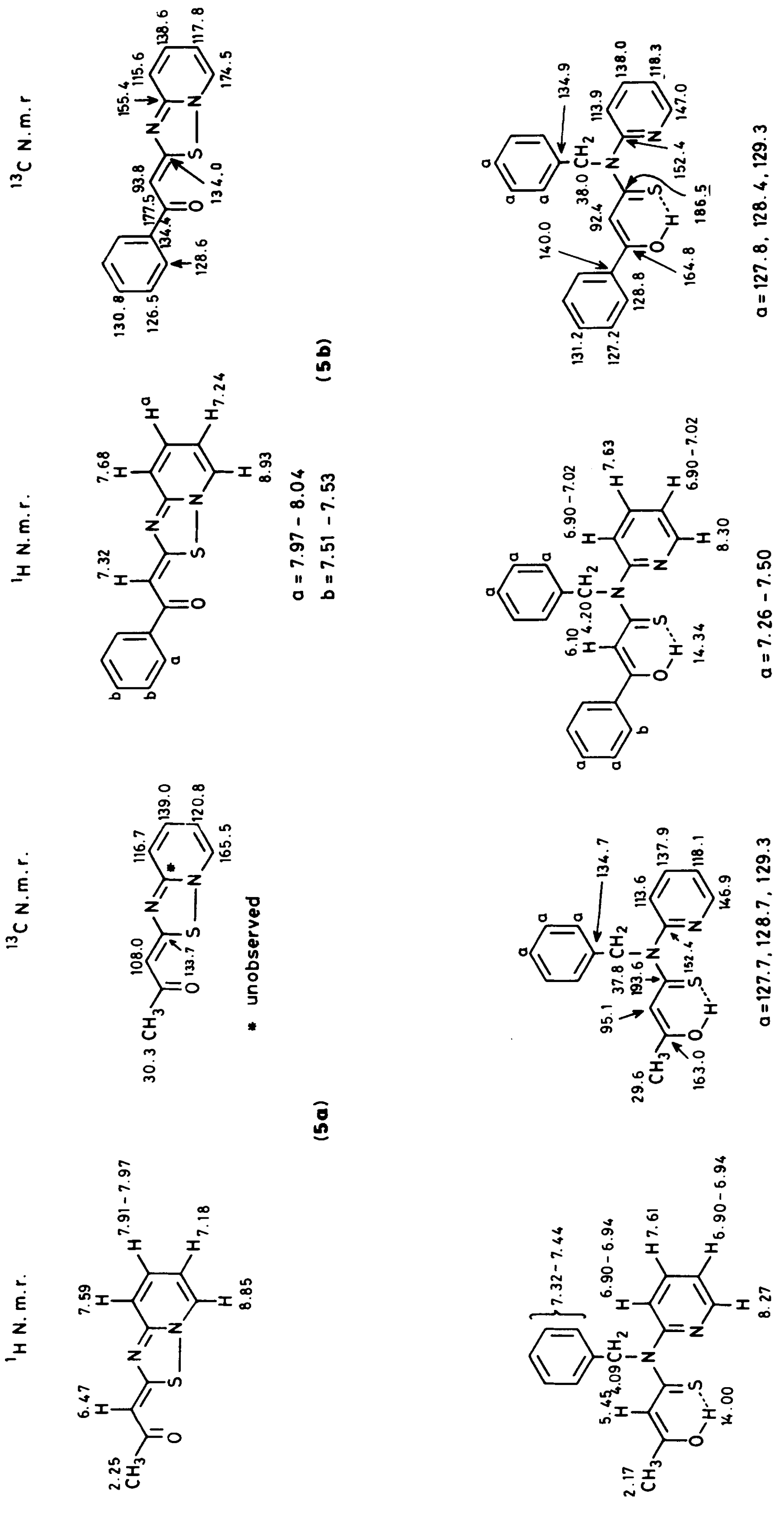


Figure 1. Proton and ^{13}C n.m.r. chemical shift data (p.p.m. relative to $SiMe_4$) for organic compounds in $CDCl_3$ [(**2a**), (**5a**), and (**5b**) in $(CD_3)_2SO$]

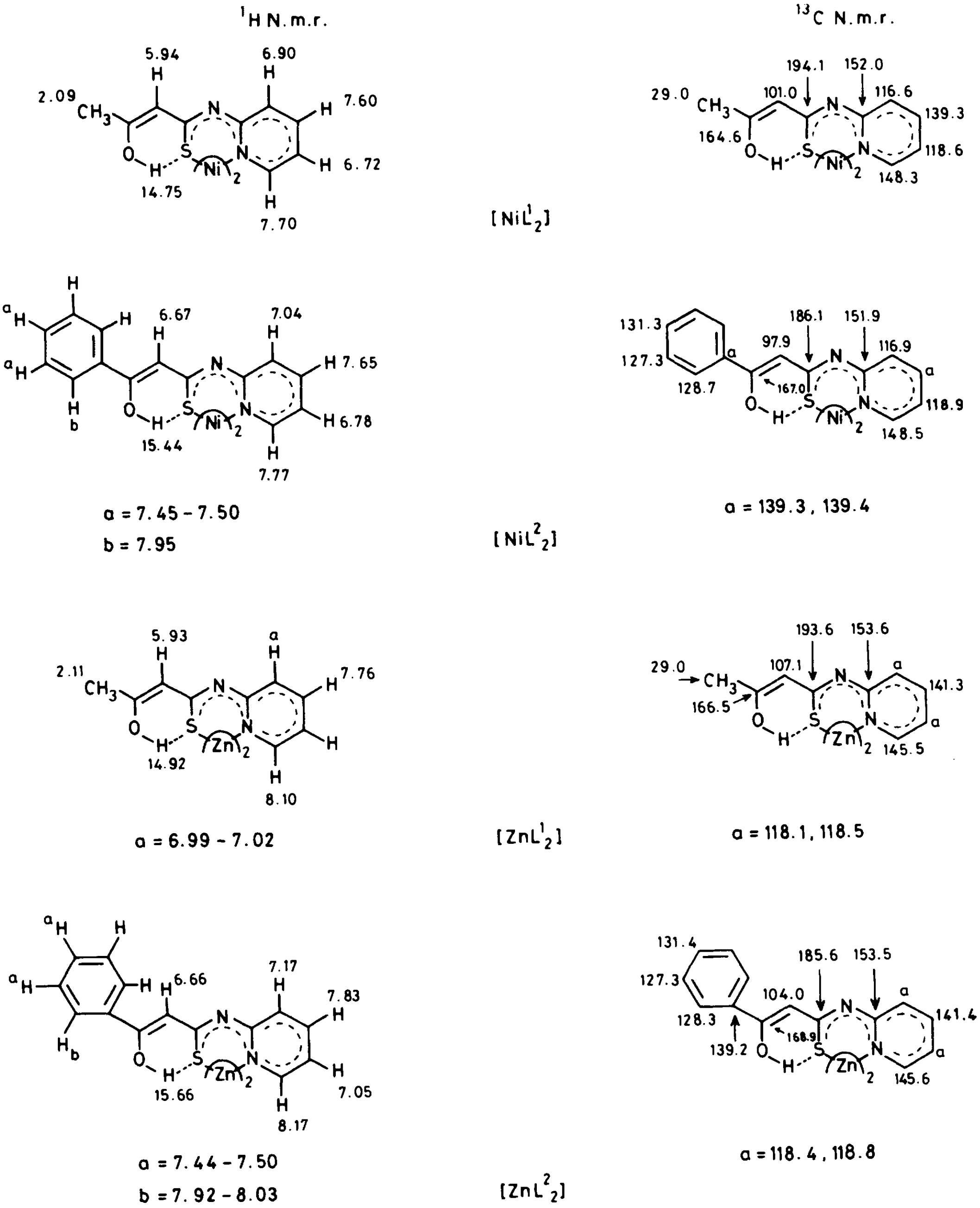


Figure 2. Proton and ^{13}C n.m.r. chemical shift data (p.p.m. relative to $SiMe_4$) for metal complexes, in $CDCl_3$

temperatures (−75 °C) by the addition of a solution of ligand to one of copper(II) acetate in the molar ratio 2:1. The complexes are stable brown powders at room temperature when filtered and dried. The i.r. spectra are almost identical with those of the nickel(II) and zinc(II) complexes. The complexes are paramagnetic and have magnetic moments of 1.74 for $[CuL^1{}_2]$ and 1.85 B.M. for $[CuL^2{}_2]$ as expected for mononuclear copper(II) complexes. However, a variable-temperature study on one of these complexes, $[CuL^2{}_2]$, shows that μ_{Cu} decreases gradually to 1.6 B.M. at *ca.* 30 K and then more rapidly to reach 0.98 B.M. at 4.2 K. Since non-interacting monomers should display Curie-like behaviour, these data suggest that weak antiferromagnetic intermolecular interactions are occurring in the solid state. The data could not be fitted to a simple Cu^{II} pair model, although a J value of -7 cm^{-1} was obtained when a sizeable contribution from monomeric Cu^{II} was included.

The e.s.r. spectra of neat powdered samples of the $[CuL_2]$ complexes showed only broad featureless resonances at $g \approx 2$. Such signals are observed in Cu^{II} complexes displaying weak intermolecular coupling. Well resolved signals due to magnetically dilute mononuclear $[CuL^2{}_2]$ were obtained, however, by doping into the $[NiL^2{}_2]$ and $[ZnL^2{}_2]$ hosts. The spectra of such samples are shown in Figures 3 and 4 together with the corresponding lineshape simulations. The spectra are markedly different because of the different geometries occurring in the Ni^{II} and Zn^{II} chromophores. The Cu^{II}/Ni^{II} spectrum is typical of a planar CuN_2S_2 system displaying N-hyperfine splitting in both the perpendicular and parallel lines.[24] The number of

Table 3. E.s.r. parameters for $[CuL^2_2]$

	g Values	Hyperfine constants (10^{-4} cm^{-1})		Linewidths (mT)
$[CuL^2_2]$ doped	$g_{\parallel} = 2.127$	$A_{\parallel}^{Cu} = 178$	$A_{\parallel}^{N} = 14$	$W_{\parallel} = 0.7$
in $[NiL^2_2]$	$g_{\perp} = 2.025$	$A_{\perp}^{Cu} = 40$	$A_{\perp}^{N} = 13$	$W_{\perp} = 0.4$
$[CuL^2_2]$ doped	$g_1 = 2.019$	$A_1^{Cu} = 75$		$W_1 = 2.1$
in $[ZnL^2_2]$	$g_2 = 2.083$	$A_2^{Cu} = 11$		$W_2 = 1.6$
	$g_3 = 2.184$	$A_3^{Cu} = 67$		$W_3 = 1.8$

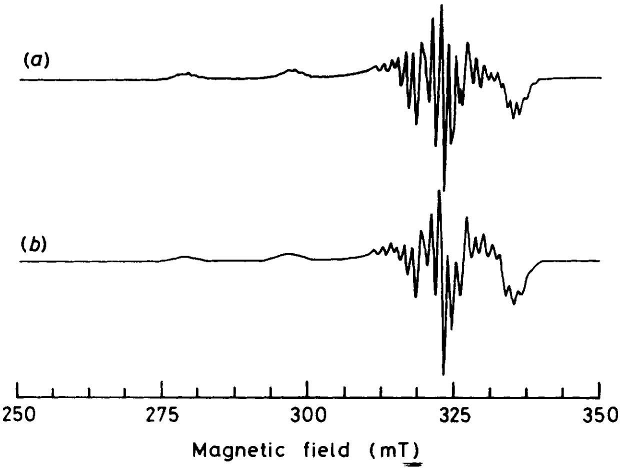


Figure 3. E.s.r. spectrum (*a*) and simulated spectrum (*b*) for $[CuL^2_2]$ doped in $[NiL^2_2]$. Microwave frequency 9.112 GHz. E.s.r. parameters are given in Table 3

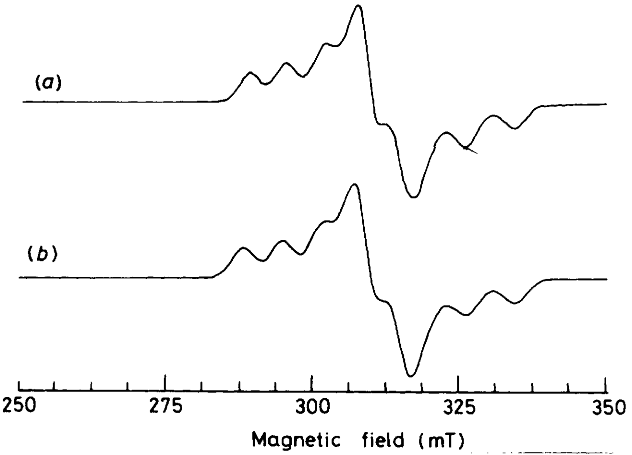


Figure 4. E.s.r. spectrum (*a*) and simulated spectrum (*b*) for $[CuL^2_2]$ doped in $[ZnL^2_2]$. Microwave frequency 9.111 GHz. E.s.r. parameters are given in Table 3

N-hyperfine lines observed on the parallel lines is due to interaction of two N atoms with the ^{63}Cu and ^{65}Cu isotopes. Contribution from both copper isotopes was allowed for in the lineshape simulation program. The best-fit g and A values are given in Table 3.

The Cu^{II}/Zn^{II} spectrum has a lineshape which is relatively rare for Cu^{II} systems and can be simulated precisely using the rhombic g and A values given in Table 3. Other recently reported systems giving rise to a large degree of rhombicity in the g and A values include $[enH_2Cl]_2[Zn[Cu]Cl_4]$ (en = ethylenediamine),[25] Zn[Cu] bis-salicylideneimines,[26] and a copper(II) methionine methyl ester complex,[27] all of which possess pseudo-tetrahedral geometry around the copper site. However, similar anisotropy is possible in distorted six-co-ordinate systems such as $K_2[Zn[Cu](H_2O)_6][SO_4]_2$.[28] A number of CuN_2S_2 thio Schiff-base complexes, doped into pseudo-tetrahedral ZnN_2S_2 host lattices have recently been reported[29,30] and these display e.s.r. lineshapes more reminiscent of the axial type (*i.e.* $g_x \approx g_y$) shown in the present Cu^{II}/Ni^{II} spectrum, with $g_{\parallel}$ and $g_{\perp}$ values similar in magnitude to those of planar analogues, but with $A_{\parallel}$ values reducéd to *ca.* 100 × 10^{-4} cm^{-1} on account of the distortions towards tetrahedral symmetry. Presumably the precise geometry around Cu in these systems is different to that in the present $[Zn[Cu]L^2_2]$ complex. The sizes of the present copper hyperfine parameters are close to the values observed in $[enH_2Cl]_2[Zn[Cu]Cl_4]$ [25] and in certain copper proteins (bonded to N, S donors).[31–33] Indeed, much of the impetus for studying the e.s.r. features of CuN_2S_2 model systems has been to mimic the low A values observed in Type 1 ('blue') copper proteins[31] and in the Cu_A site of cytochrome c oxidase.[30,32] While the present Cu^{II}/Zn^{II} spectrum and the spectra of other CuN_2S_2 model systems achieve some of the desirable features, none has so far been able to mimic all the features. The present complexes do not, of course, contain imidazole or cysteine-like RS^- donors, so the similarity in A values is probably coincidental.

Table 4. U.v.–visible spectra of the ligands (HL) and their metal complexes, $[ML_2]$, in chloroform (10^{-4}—10^{-5} mol dm^{-3}) at 295 K

Compound	$\lambda_{max.}$/nm ($\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1})
HL^1, (**4a**)	313.6 (21 400)
HL^2, (**4b**)	243.5 (12 500), 328.0br (15 900), 348.5 (16 100)
$[NiL^1_2]$	293.5 (25 300), 338.5 (32 600), 395.5 (33 700), 565.0 (760)
$[NiL^2_2]$	250.7 (26 100), 293.8 (22 400), 354.5 (29 600), 426.5 (47 500), 565.5 (1 290)
$[CuL^1_2]$*	242.0 (20 600), 326.5sh (19 900), 361.7 (30 000)
$[CuL^2_2]$*	249.0 (20 300), 387.0 (30 000)
$[ZnL^1_2]$	259.3 (18 100), 294.0 (17 200), 313br (15 700), 370.5 (57 400)
$[ZnL^2_2]$	264.0 (22 800), 299.7 (14 300), 318.0sh (12 900), 398.7 (71 600)

* Solutions change rapidly from brown to amber, indicating a possible redox reaction.

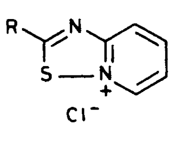
From the theoretical point of view, Hitchman[34] has recently reviewed the interpretations of hyperfine parameters in pseudo-tetrahedral copper(II) complexes and has stressed the often overlooked importance of the contribution of minor *d*-orbital components to the ground-state wave function. The rhombic g and A values for the Cu^{II}/Zn^{II} complex given in Table 3 should, in principle, provide a good test of the relationships between A values and g shifts (or coefficients of the minor *d*-orbital components) given by Hitchman and hence provide information on Cu–S and Cu–N bonding. Unfortunately the lack of single-crystal structural and spectral data does not allow us unambiguously to identify the x, y, and z components of g (and A) required to test the theory.

The u.v.–visible spectral bands observed for choroform solutions of the ligands (HL) and their metal complexes $[ML_2]$ are given in Table 4. The yellow, free ligands HL^1 and HL^2 show intense bands in the u.v. region with those of the highest energy being closer to the visible region than those of the corresponding colourless *N*-(2-pyridinyl)ketoacetamides (**1**).[1] A similar spectral shift has been observed in 2-pyridinylmethyl-ketones and -thioketones.[35] The brown $[NiL_2]$ complexes show a number of very intense and well resolved intra-ligand transitions in the region 250—426 nm, together with a visible absorption of moderate intensity at 565 nm typical of planar $\mathrm{Ni_2S_2}$ complexes.[36] The pale yellow $[\mathrm{ZnL_2}]$ complexes show very strong bands in the near-u.v. region, 370—400 nm, which are probably due to intra-ligand transitions rather than charge-transfer transitions in view of their intensities and positions. The spectra of chloroform solutions of the $[\mathrm{CuL_2}]$ complexes show only intense intra-ligand u.v. absorptions without any visible *d–d* bands. The band positions are similar to those observed for the cyclized products (**5**) (see later) suggesting that partial oxidation has occurred in these dilute solutions. The transmission spectrum of a Nujol mull of $[\mathrm{CuL^2{}_2}]$ was poorly resolved showing a strong band at 400 nm and a broad shoulder at *ca.* 750 nm.

The mononuclear metal complexes $[\mathrm{ML_2}]$ form even in the presence of excess metal ions and we have been unable to prepare any binuclear complexes analogous to those of (**1**). We believe the underlying reason for this to be the inability of (**4**) to accommodate the geometric requirement of the potential S bridge in such complexes. Although oxygen bridging atoms can readily adopt a trigonal-planar geometry, as observed[1] in the binuclear complexes of the essentially coplanar ligands (**1**), sulphur bridging atoms have rarely shown such geometry,* and would prefer to be pyramidal.[2,5] Ligands (**4**), also being essentially coplanar, would not seem to be able to allow such a geometry about the S atom and still co-ordinate in a similar fashion to (**1**).

Oxidation and Cyclization of (**4**).—It became evident quite early in our initial work on the reactions of (**4**) with copper(II) ions that the ligands are redox active and easily oxidize to (**5**). The problem is further complicated in that both unoxidized (**4**) and oxidized (**5**) forms give co-ordination compounds with $\mathrm{Cu^{II}}$ and $\mathrm{Cu^{I}}$ in reactions which show dependence on (*a*) solvent type, (*b*) concentration of reactants, (*c*) counter ion type, and (*d*) reaction temperature. Consequently, most products obtained have shown non-integer formulae and we have been unable to purify or crystallize these complexes. For example, when solutions of the ligands were mixed with solutions of copper(II) perchlorate or copper(II) nitrate in ethanol or acetone at either room temperature or -75 °C a rapid colour change from green to brown was observed in solution, and brown to light brown precipitates were obtained. The powders are near diamagnetic indicating that reduction of $\mathrm{Cu^{II}}$ to $\mathrm{Cu^{I}}$ had occurred, although it is possible that reduction was not complete. Microanalysis shows CHN ratios corresponding to (**5**) but non-integer and non-reproducible molecular formulae. Apart from bands due to $\mathrm{ClO_4}$ and $\mathrm{NO_3}$, the i.r. spectra are almost identical with those of (**5**) as are the n.m.r. and mass spectra, indicating that ligand oxidation had definitely occurred in these products.

The oxidized forms, (**5**), were synthesized independently from (**4**) using $\mathrm{K_3[Fe(CN)_6]}$ in aqueous base as oxidizing agent and have also been obtained in crystalline form from solutions of (**4**) in acetone or chloroform which have been allowed to stand in air for a few days. Heterocycles of this type have been referred to in reviews of 1,2,4-thiadiazoles[37] and their synthesis has mainly involved the oxidation of thioureas[38] and the formation of stable heterocyclic salts (see below).[39] In the case of (**5**) the nature of the enolizable R group allows the formation of a neutral entity rather than a cation. The i.r. spectra of (**5**) show less absorbance due to the pyridine ring between 1 550 and 1 600 cm^{-1} than (**4**) because much of the aromatic nature of the ring is lost in (**5**). The ν(CO) bands are observed at *ca.* 1 620 cm^{-1} and as expected there is an absence of NH bands. The n.m.r. spectra of (**5**) compare well with those of compounds containing the 2*H*-pyrido[2,3-*a*][1,2,4]thiadiazole heterocycle.[38] The mass spectra of (**5**) show molecular ion peaks of two units less than those of (**4**) and show different fragmentation patterns in which the pyridine ring, part of the heterocycle, does not fragment as a separate ion as it does in (**4**).



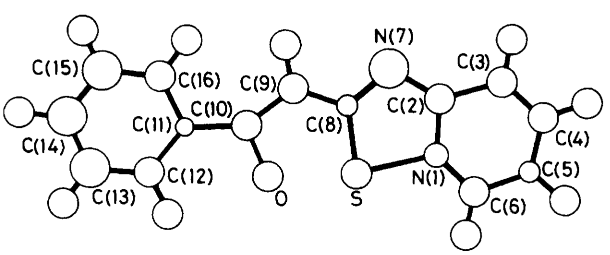


Figure 5. Molecular structure of (**5b**) with numbering scheme. Thermal ellipsoids are drawn at 50% probability level except for hydrogen atoms which have been reduced for clarity

Of particular interest to us was the predisposition of the O, S, and N atoms of (**5**) towards co-ordination with metal ions and hence a structural analysis was performed.† The structure of (**5b**) (Figure 5) shows the molecule to be almost planar with an adopted position in which the O and S atoms are brought close together [2.00(3)—2.07(3) Å separation] forming a potential O,S donor set whereas the N(7) atom is left as a potential monodentate donor. In the only other structure of a molecule containing the heterocyclic unit of (**5b**), 2-ethoxycarbonylimino-2*H*-pyrido[2,3-*a*][1,2,4]thiadiazole hydrate,[41] the molecule adopts a similar geometry to that of (**5b**), also with a strong S–O interaction (2.29 Å separation) but shows hydrogen bonding to a water molecule *via* the thiadiazole nitrogen atom [N(7)].

Redox activity of the *N*-(2-pyridinyl)thioamide unit with copper(II) has been reported and there is evidence for the formation of similar heterocycles to (**5**) on ligand oxidation.[12] Apart from the use of low reaction temperatures in the synthesis of $[\mathrm{CuL_2}]$ we have been able to eliminate the problem of oxidation and cyclization by the preparation of the *N*-benzylated derivatives (**6**) from reaction of (**4**) with benzyl chloride in aqueous base. From our preliminary work we have found these potential ligands resistant to oxidation, apparently due to the absence of the amido proton which would assist the formation of the heterocycle on deprotonation. Alkylation has commonly been employed for protection against unwanted reactions such as hydrolysis and oxidation in thiols, however these cases involved S alkylation.[42] The proton and ^{13}C n.m.r. spectra of (**6**) indicate that benzylation has occurred at the amido nitrogen and not on the sulphur presumably because of the lack of thiol character in (**4**). Compounds (**6**) adopt entirely the enol tautomeric form in chloroform solution with deshielded enol protons [14.00 for (**6a**) and 14.34 p.p.m. for (**6b**)].

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* For a recent example of a sterically constrained planar thiolate bridging sulphur see, I. G. Dance, P. J. Guerney, A. D. Rae, and M. L. Scudder, *Inorg. Chem.*, 1983, **22**, 2883.

† Suitable crystals of (**5b**) were obtained as a result of oxidation of (**4b**) in $\mathrm{CHCl_3}$–light petroleum (b.p. 40—60 °C). The crystals are hexagonal in the *R*3 (no. 146) point group. Three geometrically near-identical molecules are in each asymmetric unit, nine of which comprise each unit cell. We are currently endeavouring to solve the problem of pseudo-symmetry[40] which has arisen for this near-centrosymmetric system and has prevented full refinement (R = 0.096). The irregular atom densities in Figure 5 are a result of this problem.

Experimental

All chemicals were of laboratory grade and were used without further purification. Hydrogen sulphide gas was used without further drying. Dry hydrogen chloride gas was produced by dropping concentrated hydrochloric acid into an excess of concentrated sulphuric acid. Carbon dioxide was generated from the sublimation of solid CO_2. Acetylacetone, pyridine, and xylene were dried according to literature methods.[43] Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points were measured on a Büchi SMP-20 apparatus (those above 200 °C on an Electrothermal IA 6304 apparatus) and are uncorrected.

Infrared spectra were recorded on a Jasco IRA-1 diffraction grating spectrophotometer as Nujol mulls: s = strong, m = medium, w = weak, br = broad, and sh = shoulder. U.v.–visible spectra of chloroform solutions (10^{-4}—10^{-5} mol dm^{-3}) were recorded on a Hitachi 150-20 spectrophotometer. Proton and ^{13}C n.m.r. spectra were recorded on a Brüker AM300 multinuclear spectrometer with $SiMe_4$ as internal reference. Assignments of aromatic resonances were made on the basis of multiplicities and trends in chemical shifts reported for similar molecules.[11,13,38] Acidic protons were identified by their D_2O exchangeability. Mass spectra were measured on a VG Micromass 7070F spectrometer with an ion chamber temperature of 200 °C and an electron voltage of 70 eV (*ca.* 1.12×10^{-17} J). Unless otherwise indicated, only peaks of relative abundance greater than 10% are reported. Room-temperature magnetic susceptibilities were determined by the Faraday method on an instrument described previously.[44] Variable-temperature magnetic susceptibilities were measured as previously reported.[1] E.s.r. spectra were run at *X*-band on a Varian E12 spectrophotometer on powdered samples at liquid nitrogen temperature. Programs used for initial lineshape simulation (EPR50F) and least-squares fitting (EPR50FIT) were provided by Dr. J. Pilbrow, Physics Department, Monash University.

*4-Methyl-*2H*-pyrido*[1,2-a]*pyrimidine-2-thione* (**2a**).—*N*-(2-Pyridinyl)acetoacetamide (**1a**) (1.0 g, 5.6 mmol) was mixed with P_4S_{10} (0.50 g, 1.1. mmol) and dry pyridine (10 cm^3) was added dropwise. The mixture was heated to reflux for 1.5 h, and the dark red homogeneous mixture concentrated to half volume and slowly poured into ice–water (50 cm^3) with vigorous stirring. The dark brown-red solid which formed was filtered off and the dark red filtrate extracted with chloroform. The chloroform layer was evaporated under vacuum and the resultant residue was combined with the previously obtained solid and recrystallized from warm 95% ethanol (50 °C) and decolourizing charcoal. Concentration of the solution yielded small yellow-orange needles (0.28 g, 28%). $\nu_{max.}$ 1 620s(br), 1 520m, 1 335s, 1 300s, 1 280s, 1 130s, 1 105s, 990m, 910m, 850m, 770s cm^{-1}; *m*/*z* 176 (M^+, 100%), 136 (11), 132 (53), 131 (32), 79 (11), 78 (75), 51 (23), 39 (13). The above method was used to prepare 4-phenyl-2*H*-pyrido[1,2-*a*]pyrimidine-2-thione (**2b**) (0.14 g, 28%) from *N*-(2-pyridinyl)benzoylacetamide (**1b**). This compound however was not obtained analytically pure and remained as a hygroscopic tarry orange solid. The structure was inferred from the mass spectral data. M.p. 135—140 °C; *m*/*z* 238 (M^+, 100%), 237 (20), 194 (55), 179 (20), 136 (36), 135 (37), 121 (11), 105 (34), 102 (31), 94 (53), 78 (21), 77 (10), 67 (21).

N-(2-*Pyridinyl*)*thiobenzoylacetamide Hydrochloride Hydrate* (**3**).—Hydrogen sulphide was passed through a solution of *N*-(2-pyridinyl)benzoylacetamide (**1b**) (1.0 g, 4.2 mmol) in ethanol (50 cm^3) for 20 min, with the temperature kept constant at − 10 °C. Dry hydrogen chloride gas was then passed through the reaction mixture for 25 min. The reaction flask was subsequently fitted with a calcium chloride drying tube and left standing at room temperature overnight (15 h). The resultant dark amber mixture was poured into ice–water (100 cm^3). After standing (1 d) fine lemon-yellow needles formed which were filtered off and dried in air (0.52 g, 39%). $\nu_{max.}$ 3 440m(br), 3 320m(br), 1 650s, 1 630m, 1 600m(br), 1 570s(br), 1 500m, 1 490m, 1 300m(br), 1 260m, 1 230m, 1 210m, 1 180s, 1 150s, 850s, 810m, 780s, 760s, 680m cm^{-1}; *m*/*z* 256 [M^+ − (HCl, $\frac{3}{2}$ H_2O), 26%], 223 (25), 163 (12), 162 (13), 134 (38), 121 (35), 103 (14), 102 (12), 95 (24), 94 (100), 91 (14), 78 (22), 77 (13), 67 (21), 51 (13).

Synthesis of Ligands HL^1 *and* HL^2.—N-(2-*Pyridinyl*)*acetothioacetamide* (**4a**).—Dry acetylacetone (10.0 g, 0.100 mol) was added dropwise to sodium spheres (2.30 g, 0.100 mol) in anhydrous diethyl ether (100 cm^3), with stirring, under an atmosphere of nitrogen. A fine white precipitate began to form during the addition. The reaction was stirred for 24 h, whereupon almost all the sodium had reacted.

Separately, a solution of pure *S*-methyl *N*-(2-pyridinyl)-dithiocarbamate[19] (18.4 g, 0.100 mol) in dry xylene (400 cm^3) was heated to reflux for at least 3 h under a stream of nitrogen. The methanethiol evolved was swept with nitrogen into an aqueous solution of lead(II) acetate whereby the progress of the reaction was monitored and the methanethiol trapped with the formation of yellow $Pb(SCH_3)_2$. (**CAUTION**: efficient ventilation required.) After the evolution of methanethiol had ceased the resultant amber xylene solution of 2-isothiocyanatopyridine was reduced to 100 cm^3, cooled in an ice–water bath and immediately added dropwise, with stirring, to the sodium acetylacetone mixture prepared above. (The isothiocyanate in solution slowly converts to the orange dimer[45] if left standing.)

The resultant yellow mixture was stirred for 3 d under a nitrogen atmosphere. Ice–water (100 cm^3) was added whereupon the bright yellow precipitate dissolved in the aqueous phase. The organic phase was extracted with a minimum amount of 10% potassium hydroxide solution and the combined aqueous phases were stirred with a total of 200 cm^3 of 10% aqueous potassium hydroxide solution for 3 h at room temperature. The resultant amber solution was filtered off, cooled in ice, and slowly neutralized by passing carbon dioxide into the cooled solution with stirring (2 h). The pale yellow precipitate formed was filtered off, dried in air, and recrystallized from warm ethanol–water. Yield 7.0 g, 36%. The dry compound was kept refrigerated as it shows long term thermal instability at room temperature. $\nu_{max.}$ 3 180m, 3 130m, 1 720m, 1 615s, 1 595m, 1 575s, 1 515s, 1 325s, 1 305s, 1 290s, 1 280m, 1 200s, 1 165m, 1 150m, 1 010m, 990m, 940m, 840m, 810m, 760m, 735m cm^{-1}; *m*/*z* 194 (M^+, 42%), 152 (11), 151 (100), 137 (26), 119 (23), 118 (13), 94 (31), 78 (75), 67 (18), 51 (19), 43 (46).

The above method was also used in the preparation of *N*-(2-pyridinyl)benzoylthioacetamide (**4b**) as a bright yellow solid (10.5 g, 41%). In this case dibenzoylmethane (22.4 g, 0.100 mol) was dissolved in warm anhydrous diethyl ether (150 cm^3), the solution filtered and added to sodium spheres (2.30 g, 0.100 mol) in anhydrous diethyl ether (25 cm^3) with stirring as above. $\nu_{max.}$ 3 200m, 3 120m, 1 610m(sh), 1 600m(sh), 1 580s(br), 1 570s(sh), 1 540s(br), 1 490s, 1 440s, 1 320s, 1 290s, 1 255s, 1 195s, 1 170m, 1 140s, 1 080m, 1 050m, 1 010m, 980m, 820m, 770m, 740s, 710s, 670s cm^{-1}; *m*/*z* 256 (M^+, 22%), 223 (13), 152 (10), 151 (100), 137 (27), 136 (15), 121 (10), 105 (97), 94 (16), 78 (59), 77 (77), 51 (35).

Synthesis of Complexes $[ML^1{}_2]$ *and* $[ML^2{}_2]$. M = Ni^{II} *or* Zn^{II}. A solution of the ligand [*ca.* 100 mg of (**4a**) or (**4b**)] in warm ethanol (5 cm^3, 50 °C) was added to a solution of the appropriate metal acetate, nickel(II) acetate tetrahydrate or zinc(II) acetate dihydrate, in warm ethanol (5 cm^3) with a ligand to metal molar ratio of 2:1. The resultant maroon and amber solutions respectively yielded dark brown microcrystals and yellow flakes on cooling. The solids were filtered off, washed with cold ethanol (5 cm^3), dried initially in air, and then *in vacuo* over P_2O_5. Yields were always above 90%.

M = Cu^{II}. These reactions were performed with cooling in an acetone–dry ice bath. A solution of the ligand [*ca.* 100 mg of (**4a**) or (**4b**)] in the minimum of AR acetone was added slowly with stirring to a filtered solution of copper(II) acetate monohydrate in the minimum of AR acetone, with a ligand to metal molar ratio of 2:1. Dark green solutions were immediately obtained and kept cold for *ca.* 5 h whereby a dark brown precipitate formed. Precipitation was found to be encouraged by bubbling nitrogen into the reaction mixtures during this time. The precipitates were filtered off cold, dried initially in air, then *in vacuo* over P_2O_5. Yields: $[CuL^1{}_2]$ 28%, $[CuL^2{}_2]$ 67%. The doped complexes were prepared in a similar manner using a metal ion solution with a 5:95% ratio of copper(II) to nickel(II) or zinc(II).

The i.r. spectra of complexes derived from the same ligands were very similar. The following i.r. spectra of the copper(II) complexes are representative of those of the other complexes: $[CuL^1{}_2]$, $\nu_{max.}$ 1 615s, 1 600s, 1 575s, 1 540s, 1 490s, 1 415s, 1 355m, 1 340m, 1 285s, 1 235s, 1 165s, 1 155s, 1 020m, 990m, 895m, 875m, 840m, 795s, 775s, 760m, 740m cm^{-1}; $[CuL^2{}_2]$, $\nu_{max.}$ 1 620s, 1 600s, 1 580s, 1 550s, 1 530s, 1 485s, 1 410s, 1 345m, 1 305s, 1 290s, 1 250s, 1 180m, 1 160s, 1 010m, 960w, 880w, 840w, 795w, 765s, 745s cm^{-1}.

*2-Acetonylidene-*2H*-pyrido*[2,3-a][1,2,4]*thiadiazole* (**5a**).—A solution of *N*-(2-pyridinyl)acetothioacetamide (**4a**) (0.100 g, 0.515 mmol) in the minimum volume of 95% ethanol was added to a warm solution of $K_3[Fe(CN)_6]$ (0.338 g, 1.03 mmol) in 10% aqueous sodium hydroxide (20 cm^3) with stirring and warming for 0.5 h. The mixture was cooled in ice, neutralized with 2 mol dm^{-3} HCl and extracted into chloroform. The chloroform fraction was dried with Na_2SO_4, filtered, and a brown solid precipitated on the dropwise addition of anhydrous diethyl ether–light petroleum (b.p. 40—60 °C). The solid was filtered off and dried *in vacuo* over P_2O_5. Yield 0.020 g, 20%. $\nu_{max.}$ 1 625s, 1 600w(sh), 1 545s(sh), 1 530s(br), 1 515s(sh), 1 500m(sh), 1 445s, 1 350s, 1 325s, 1 290m, 1 270s, 1 200s, 1 180m, 1 135s, 1 110m, 1 020s, 1 000m, 970s, 870w, 850w, 805m, 760s, 730s, 710s, 680m cm^{-1}; $\lambda_{max.}$ 241.5 (ε 8 000), 255.7 (7 800), 294.7sh (6 000), 321.3 (8 500), 355.3 nm (10 000 dm^3 mol^{-1} cm^{-1}); *m/z* 192 (M^+, 76%), 178 (10), 177 (100), 105 (46), 78 (69), 51 (28), 45 (13), 43 (28).

The above method was also used in the preparation of 2-benzoylmethylidene-2*H*-pyrido[2,3-*a*][1,2,4]thiadiazole (**5b**) from *N*-(2-pyridinyl)benzoylthioacetamide (**4b**). However, in this case the chloroform fraction was evaporated under vacuum and the residue recrystallized from warm 95% ethanol to give bright yellow flaky needles. Yield 22%. $\nu_{max.}$ 1 620m, 1 590w(sh), 1 530s, 1 505s(sh), 1 360s, 1 330s, 1 265m, 1 215m, 1 200m, 1 150m, 1 080m, 1 020m, 905w, 865w, 770m, 755s, 740m, 725m, 715m, 690m cm^{-1}; $\lambda_{max.}$ 247.2 (ε 15 500), 382.0 nm (22 000 dm^3 mol^{-1} cm^{-1}); *m/z* 254 (M^+, 100%), 177 (56), 150 (14), 145 (24), 113 (13), 105 (55), 78 (51), 77 (40), 51 (24).

N-*Benzyl-*N-*(2-pyridinyl)acetothioacetamide* (**6a**).—To a solution of *N*-(2-pyridinyl)acetothioacetamide (**4a**) (1.0 g, 5.1 mmol) in 2 mol dm^{-3} NaOH (5 cm^3) and ethanol (5 cm^3) benzyl chloride (0.65 g, 5.1 mmol) was added dropwise with stirring. An off-white precipitate formed rapidly. The mixture was stirred for 0.5 h, neutralized with 2 mol dm^{-3} HCl, the precipitate filtered off, washed with ethanol and diethyl ether and dried in air. The shiny off-white flakes (0.91 g, 63%) have a pungent odour. $\nu_{max.}$ 1 615s, 1 595s, 1 585s, 1 555s, 1 505m, 1 485s, 1 440m, 1 425s, 1 355m, 1 315m, 1 290s, 1 270m, 1 255m, 1 235s, 1 170w, 1 150s, 1 140w, 1 070w, 1 030w, 990w, 950w, 900w, 865m, 850m, 780s, 765w, 740s, 735m, 720m, 700s cm^{-1}; *m/z* 284 (M^+, <1%), 251 (4), 241 (5), 193 (57), 151 (19), 145 (16), 124 (15), 119 (35), 91 (83), 79 (20), 78 (100), 65 (16), 51 (28), 43 (29), 40 (48).

The above method was also used in the preparation of *N*-benzyl-*N*-(2-pyridinyl)benzoylthioacetamide (**6b**) from *N*-(2-pyridinyl)benzoylthioacetamide (**4b**) as a pale yellow powder. Yield 60%. $\nu_{max.}$ 1 615s, 1 590s, 1 565s(sh), 1 555s(br), 1 495s, 1 485s, 1 425s, 1 315s, 1 300s, 1 290s, 1 280s(sh), 1 255s, 1 230m, 1 205m, 1 180m, 1 160s, 1 150m(sh), 1 085m, 1 070m, 1 030m, 995m, 900w, 870m, 845s(br), 805w, 775s, 745s, 735s, 720m, 710m, 700m, 655m cm^{-1}; *m/z* 346 (M^+, <1%), 313 (2), 255 (34), 121 (11), 105 (100), 91 (48), 79 (14), 78 (33), 77 (42), 51 (17).

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