Synthetic, Spectroscopic, and *X*-Ray Crystallographic Studies on Binuclear Copper(II) Complexes with a Tridentate NNS-bonding 2-Formylpyridine Thiosemicarbazone Ligand. The Characterization of Both Neutral and Deprotonated Co-ordinated Ligand Structures†

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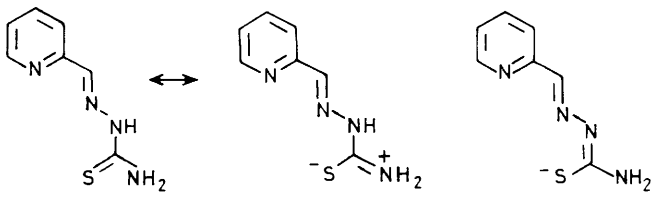
The preparation of the complexes $[(CuLX)_2]$ (HL = 2-formylpyridine thiosemicarbazone) from the interaction of HL with the appropriate copper salt (X = CH_3COO, Cl, NO_3, or ClO_4) or by reaction of an HL–KX mixture with copper(II) acetate monohydrate (X = Br or I) is described. Dissolution of $[\{CuL(CH_3COO)\}_2]$ in H_2SO_4 or HCl yields the protonated ligand complexes $[\{Cu(HL)(SO_4)\}_2]$ and $[\{Cu(HL)Cl_2\}_2]\cdot 2H_2O$ respectively. The complexes have been characterized by a variety of spectroscopic techniques and the crystal and molecular structures of $[\{CuL(CH_3COO)\}_2]$ and $[\{Cu(HL)(SO_4)\}_2]$ determined by single-crystal *X*-ray diffraction techniques from diffractometer data. Crystals of $[\{CuL(CH_3COO)\}_2]$ are triclinic, space group $P\bar{1}$, with $a = 8.827(3)$, $b = 8.813(3)$, $c = 8.997(3)$ Å, $\alpha = 117.49(2)$, $\beta = 110.96(3)$, $\gamma = 91.65(3)^\circ$, and $Z = 1$. Crystals of $[\{Cu(HL)(SO_4)\}_2]$ are monoclinic, space group $C2/c$, with $a = 14.751(3)$, $b = 9.138(2)$, $c = 17.468(4)$ Å, $\beta = 104.91(2)^\circ$, and $Z = 4$. After full-matrix least-squares refinement the final R value was 0.027 for both complexes (2 216 and 2 206 observed reflections were used respectively). Both complexes consist of discrete centrosymmetric dimers, the monomeric units being bridged by two acetato or sulphato ligands. The copper atoms have a distorted square-pyramidal co-ordination geometry with three donor atoms (NNS) coming from L or HL to form a tricyclic ligating system. The fourth donor atom (oxygen) comes from the bridging CH_3COO^- or SO_4^{2-} ion. The fifth co-ordination position is occupied by a less strongly bound oxygen from the second bridging anion.

Extensive literature on the antitumour properties of many α-*N*-heterocyclic carboxaldehyde thiosemicarbazones is now available.[1–4] It is postulated that these ligands act as NNS tridentates which bind to iron at the active site of ribonucleotide reductase, a key enzyme in the synthesis of precursors of DNA.[4,5] Also a number of thiosemicarbazones and their copper and iron complexes have been incubated with Ehrlich cells and then injected into mice.[6–8] Some iron and copper complexes were found to be active in cell destruction, as well as in the inhibition of DNA synthesis, whereas the free ligands were not as potent.

One of the ligands used in these studies was 2-formylpyridine thiosemicarbazone (HL) and its copper complex was formulated as $CuL(CH_3COO)$.[6,9] The biochemical and cellular reactivity of this compound has been discussed elsewhere.[10–13] As an aid to the understanding of such processes we have undertaken a single-crystal *X*-ray structure analysis on the complex $CuL(CH_3COO)$, the active precursor, and find that it is in fact a dimer, *viz*. $[\{CuL(CH_3COO)\}_2]$. A spectroscopic study on this complex in the solid state has been performed, and a later paper will concentrate on solution studies. In addition, here we extend the range of derivatives that have been prepared; compounds of the type $[\{CuLX\}_2]$ (X = Cl, Br, I, NO_3, or ClO_4) are reported. Also the nature of the compound previously wrongly formulated as $CuL(HSO_4)$[14] has been reinvestigated. A single-crystal *X*-ray structure analysis on this compound shows that it should be formulated as $[\{Cu(HL)(SO_4)\}_2]$, the ligand being remarkably in the neutral non-deprotonated form.



(a) (b)
HL L

Experimental

Magnetic moments were measured by the Faraday method with a Bruker BM4 magnet in conjunction with a Sartorious 7085 microbalance. The standard used was $Hg[Co(SCN)_4]$ and diamagnetic corrections were made using Pascal's constants. Reflectance spectra were recorded on a Beckman Acta MIV instrument with a standard reflectance attachment. Infrared spectra, recorded as KBr or CsI discs, were obtained using Beckman IR 4250 (4 000—250 cm^{-1}) or Perkin-Elmer 180 (500—150 cm^{-1}) spectrometers. Electron spin resonance spectra were recorded, for frozen solutions or solids, at 110 K on a Varian E-104A spectrometer fitted with a Varian E-257 variable-temperature control unit. Spectral *g* values were calibrated with a diphenylpicrylhydrazyl (dpph) standard. Raman spectra were obtained for rotating solid samples mounted on KBr using Coderg T 800 (λ_{ex} = 488.0 and 514.5 nm) or Ramalog V (λ_{ex} = 676.4 nm) spectrometers. Peak areas were determined by using the trace cut and weigh technique. The intensities were standardised by relating the individual peak areas to that of a peak adjudged to show little variation on excitation with the different laser lines. A band at *ca*. 295 cm^{-1}

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Analytical, magnetic, and electronic spectral data

		Analyses (%)[a]				Absorption maxima (nm)[c]	
Complex	Colour	C	H	N	$\mu_{eff.}$[b]	Charge transfer	d-d
$[\{CuL(CH_3COO)\}_2]$	Dark green	35.6 (35.8)	3.6 (3.3)	18.5 (18.6)	1.88	416	640
$[(CuLCl)_2]$	Green	30.1 (30.2)	2.8 (2.5)	20.1 (20.1)	1.88	412	623
$[(CuLBr)_2]$	Brown	26.8 (26.05)	2.5 (2.2)	18.3 (17.4)	1.83	418	652
$[(CuLI)_2]$	Brown	23.6 (22.7)	2.2 (1.9)	15.6 (15.2)	1.78	427	630 (sh)
$[\{CuL(NO_3)\}_2]$	Brown	27.5 (27.6)	2.8 (2.3)	22.3 (23.0)	1.42	395, 500 (sh)	650 (sh)
$[\{CuL(ClO_4)\}_2]$	Brown	24.6 (24.6)	2.6 (2.1)	15.7 (16.4)	1.34	381, 495 (sh)	640 (sh)
$[\{Cu(HL)(SO_4)\}_2]$	Blue green	24.7 (24.7)	2.6 (2.4)	16.45 (16.5)	1.86	360 (sh)	700
$[\{Cu(HL)Cl_2\}_2]\cdot 2H_2O$	Pale green	25.1 (25.3)	3.0 (3.0)	16.45 (16.8)	1.86	*ca.* 400 (sh)	725

[a] Calculated values given in parentheses. [b] Measured at 293 K. [c] Reflectance spectra.

Table 2. Final atomic co-ordinates for $[\{CuL(CH_3COO)\}_2]$ with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu	0.042 17(3)	0.167 90(3)	0.461 81(3)	C(7)	0.326 6(3)	0.246 4(3)	0.382 1(3)
S(1)	0.181 63(8)	0.053 23(7)	0.281 02(8)	C(8)	0.274 8(3)	0.046 5(3)	0.776 3(3)
O(1)	0.137 5(2)	0.038 8(2)	0.655 9(2)	C(9)	0.419 3(4)	0.193 1(4)	0.874 4(5)
O(2)	0.292 6(3)	−0.057 2(3)	0.832 9(3)	H(1)	−0.244(3)	0.205(4)	0.595(3)
N(1)	−0.051 5(2)	0.341 1(2)	0.635 0(2)	H(2)	−0.323(4)	0.412(4)	0.800(4)
N(2)	0.207 2(2)	0.387 3(2)	0.571 7(2)	H(3)	−0.151(3)	0.699(4)	0.973(4)
N(3)	0.333 1(2)	0.399 6(2)	0.521 6(3)	H(4)	0.082(3)	0.757(3)	0.922(3)
N(4)	0.440 8(3)	0.245 9(3)	0.317 2(4)	H(5)	0.251(3)	0.640(4)	0.745(4)
C(1)	−0.184 5(3)	0.313 1(3)	0.663 7(3)	H(6)	0.504(4)	0.334(4)	0.365(4)
C(2)	−0.225 9(3)	0.446 0(4)	0.792 0(4)	H(7)	0.430(4)	0.151(4)	0.215(4)
C(3)	−0.126 7(3)	0.613 5(3)	0.892 9(3)	H(8)	0.401(4)	0.293(4)	0.872(4)
C(4)	0.010 7(3)	0.645 5(3)	0.863 1(3)	H(9)	0.439(5)	0.170(6)	0.751(6)
C(5)	0.045 0(3)	0.506 1(3)	0.733 3(3)	H(10)	0.507(5)	0.205(5)	0.930(5)
C(6)	0.186 3(3)	0.527 9(3)	0.692 4(3)				

Table 3. Final atomic co-ordinates for $[\{Cu(HL)(SO_4)\}_2]$ with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu	0.309 65(2)	0.127 63(3)	0.462 85(2)	C(3)	0.568 8(2)	0.097 9(3)	0.691 1(2)
S(1)	0.213 08(5)	0.062 41(7)	0.343 63(4)	C(4)	0.524 7(2)	−0.023 8(3)	0.650 8(2)
S(2)	0.177 29(5)	0.059 54(6)	0.597 83(3)	C(5)	0.451 7(2)	−0.002 8(3)	0.584 3(2)
O(1)	0.209 0(1)	0.164 0(2)	0.542 5(1)	C(6)	0.400 8(2)	−0.121 8(3)	0.536 3(2)
O(2)	0.113 1(2)	0.137 4(2)	0.634 3(1)	C(7)	0.230 4(2)	−0.121 4(3)	0.355 1(2)
O(3)	0.131 9(1)	−0.063 7(2)	0.548 5(1)	H(1)	0.449(2)	0.341(3)	0.574(1)
O(4)	0.261 0(2)	0.008 4(2)	0.655 8(1)	H(2)	0.571(2)	0.322(3)	0.685(2)
N(1)	0.423 7(2)	0.133 5(2)	0.556 6(1)	H(3)	0.611(2)	0.087(3)	0.732(2)
N(2)	0.335 2(2)	−0.081 7(2)	0.477 0(1)	H(4)	0.540(2)	−0.117(3)	0.666(2)
N(3)	0.284 5(2)	−0.179 3(2)	0.423 5(1)	H(5)	0.418(2)	−0.220(3)	0.547(2)
N(4)	0.193 5(2)	−0.215 6(3)	0.299 4(2)	H(6)	0.303(3)	−0.266(4)	0.430(2)
C(1)	0.467 3(2)	0.249 3(3)	0.594 8(2)	H(7)	0.210(2)	−0.311(4)	0.308(2)
C(2)	0.540 8(2)	0.234 9(4)	0.663 3(2)	H(8)	0.169(3)	−0.183(4)	0.261(2)

was used for $[\{CuL(CH_3COO)\}_2]$ and $[\{CuLCl\}_2]$ and a doublet at *ca.* 305 cm^{-1} for $[\{Cu(HL)(SO_4)\}_2]$.

The ligand HL was synthesised following a published method.[15] Microanalyses were performed by the Microanalytical Laboratory, Faculty of Chemistry, University of Bielefeld. Analytical data are summarised in Table 1.

Crystallography.—A similar procedure was used for the data collection and structure determination for both the complexes $[\{CuL(CH_3COO)\}_2]$ and $[\{Cu(HL)(SO_4)\}_2]$.

Crystal data for $[\{CuL(CH_3COO)\}_2]$. $C_{18}H_{20}Cu_2N_8O_4S_2$, $M = 603.6$, triclinic, $a = 8.827(3)$, $b = 8.813(3)$, $c = 8.997(3)$ Å, $\alpha = 117.49(2)$ $\beta = 110.96(3)$, $\gamma = 91.65(3)°$, $U = 563.7$ Å^3 [by least-squares refinement of the angular settings of 15 high-angle reflections ($20 < 2\theta < 30°$), $\lambda = 0.710\,69$ Å], space group $P\bar{1}$, $Z = 1$, $D_c = 1.78$ g cm^{-3}. Dark green platelets; crystal size 0.1 × 0.3 × 0.5 mm, $\mu(Mo\text{-}K_\alpha) = 21.13$ cm^{-1}.

Crystal data for $[\{Cu(HL)(SO_4)\}_2]$. $C_{14}H_{16}Cu_2N_8O_8S_4$, $M = 679.7$, monoclinic, $a = 14.751(3)$, $b = 9.138(2)$, $c = 17.468(4)$ Å, $\beta = 104.91(2)°$, $U = 2\,275.3$ Å^3 [by least-squares refinement of the angular settings of 15 high-angle reflections ($20 < 2\theta < 30°$), $\lambda = 0.710\,69$ Å], space group $C2/c$, $Z = 4$, $D_c = 1.98$ g cm^{-3}. Blue-green rhombohedra; crystal size 0.2 × 0.3 × 0.4 mm, $\mu(Mo\text{-}K_\alpha) = 24.68$ cm^{-1}.

Data collection and processing. Syntex $P2_1$ four-circle diffractometer, ω scan with graphite-monochromated Mo-K_α radiation, 2θ range 4—54°; scan 1° in ω bisected by $K_{\alpha 1,2}$ maximum; scan speed 3.5—29.3° min^{-1}; background/scan time scan ratio 0.66; 1 reference reflection every 39 reflections measured; 2 686 reflections measured for $[\{CuL(CH_3COO)\}_2]$, 2 216 unique; 2 803 reflections measured for $[\{Cu(HL)(SO_4)\}_2]$, 2 206 unique [$F_o > 3.92\sigma(F_o)$]; data corrected for Lorentz and polarization effects; empirical absorption correction applied for $[\{Cu(HL)(SO_4)\}_2]$.

Table 4. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for the complexes $[\{CuL(CH_3COO)\}_2]$ and $[\{Cu(HL)(SO_4)\}_2]$*

(*a*) Bond lengths

	$[\{CuL(CH_3COO)\}_2]$		$[\{Cu(HL)(SO_4)\}_2]$		$[\{CuL(CH_3COO)\}_2]$		$[\{Cu(HL)(SO_4)\}_2]$
Cu–N(1)	2.059(2)		2.024(2)	N(3)–C(7)	1.335(3)		1.362(3)
Cu–N(2)	1.970(2)		1.953(2)	N(4)–C(7)	1.333(4)		1.309(3)
Cu–S(1)	2.274(1)		2.279(1)	C(1)–C(2)	1.384(4)		1.399(4)
Cu–O(1′)	1.951(1)		1.922(2)	C(2)–C(3)	1.375(4)		1.368(4)
Cu–O(1)	2.427(2)		2.306(2)	C(3)–C(4)	1.381(5)		1.385(4)
N(1)–C(1)	1.329(4)		1.326(3)	C(4)–C(5)	1.384(3)		1.380(3)
N(1)–C(5)	1.350(2)		1.361(3)	C(5)–C(6)	1.451(4)		1.457(3)
N(2)–N(3)	1.359(3)		1.366(3)	C(7)–S(1)	1.725(2)		1.703(3)
N(2)–C(6)	1.290(3)		1.277(3)				
Acetate and sulphate bond lengths							
C(8)–O(1)	1.279(3)	S(2)–O(1)	1.515(2)				
C(8)–O(2)	1.224(4)	S(2)–O(2)	1.456(2)				
C(8)–C(9)	1.506(4)	S(2)–O(3)	1.470(2)				
		S(2)–O(4)	1.458(2)				
(*b*) Bond angles							
N(1)–Cu–N(2)	80.6(1)		80.2(1)	Cu–N(2)–N(3)	124.3(1)		120.0(1)
N(1)–Cu–S(1)	162.6(1)		160.1(1)	C(6)–N(2)–N(3)	119.3(2)		122.3(2)
N(1)–Cu-O(1′)	96.7(1)		95.3(1)	Cu–S(1)–C(7)	95.8(1)		96.4(1)
N(1)–Cu–O(1)	91.6(1)		92.2(1)	C(1)–C(2)–C(3)	119.0(3)		119.1(3)
N(2)–Cu–S(1)	83.2(1)		85.1(1)	C(2)–C(3)–C(4)	119.4(3)		119.7(2)
N(2)–Cu–O(1′)	174.5(1)		175.4(1)	C(3)–C(4)–C(5)	118.4(2)		118.6(3)
N(2)–Cu–O(1)	108.2(1)		101.4(1)	C(4)–C(5)–N(1)	122.3(2)		121.8(2)
S(1)–Cu–O(1′)	98.9(1)		99.6(1)	C(4)–C(5)–C(6)	122.1(2)		123.7(2)
S(1)–Cu–O(1)	99.5(1)		104.0(1)	N(1)–C(1)–C(2)	122.4(2)		121.6(2)
O(1′)–Cu–O(1)	76.5(1)		77.3(1)	N(1)–C(5)–C(6)	115.6(2)		114.4(2)
Cu–O(1)–Cu′	103.5(1)		102.7(1)	C(5)–C(6)–N(2)	116.3(2)		115.1(2)
Cu–N(1)–C(1)	130.3(1)		128.5(2)	N(2)–N(3)–C(7)	111.7(2)		116.1(2)
Cu–N(1)–C(5)	111.2(2)		112.1(2)	N(3)–C(7)–S(1)	124.8(2)		121.5(2)
C(1)–N(1)–C(5)	118.5(2)		119.2(2)	N(3)–C(7)–N(4)	116.5(2)		115.8(2)
Cu–N(2)–C(6)	116.3(2)		117.7(2)	S(1)–C(7)–N(4)	118.7(2)		122.7(2)
Acetate and sulphate bond angles							
Cu–O(1)–C(8)	137.9(2)	Cu–O(1)–S(2)	130.3(1)	O(1)–C(8)–C(9)	115.9(3)	O(1)–S(2)–O(4)	107.4(1)
Cu′–O(1)–C(8)	116.4(2)	Cu′–O(1)–S(2)	126.3(1)	O(2)–C(8)–C(9)	120.3(2)	O(2)–S(2)–O(3)	112.4(1)
O(1)–C(8)–O(2)	123.8(2)	O(1)–S(2)–O(2)	108.3(1)			O(2)–S(2)–O(4)	112.5(1)
		O(1)–S(2)–O(3)	106.1(1)			O(3)–S(2)–O(4)	109.8(1)

* C–H bond lengths 0.83—0.94 Å, mean 0.91 Å; N–H bond lengths 0.73—0.91 Å, mean 0.83 Å.

Structure analysis and refinement. The structures were solved by direct methods (SHELXTL program package). After location of the non-hydrogen atoms the least-squares refinement (all atoms were refined anisotropically) converged to $R\,(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ values of 0.036 for $[\{CuL(CH_3COO)\}_2]$ and 0.035 for $[\{Cu(HL)(SO_4)\}_2]$. A following difference-Fourier map showed several maxima which clearly could be assigned to the hydrogen atoms. After their inclusion in the refinement procedure (all hydrogen atoms were refined with individual isotropic thermal parameters) the final R values improved to 0.027 for both structures and $R'\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ values were 0.034 for $[\{CuL(CH_3COO)\}_2]$ and 0.031 for $[\{Cu(HL)(SO_4)\}_2]$. In the final difference map of $[\{CuL(CH_3COO)\}_2]$ no electron density was detected which could be attributed to a hydrogen atom attached to N(3), although all other hydrogen atoms had previously been easily located.

Anomalous dispersion corrections were applied to all atoms. Fractional atomic co-ordinates are given in Tables 2 and 3 and bond lengths and angles in Table 4.

Preparation of the Copper Complexes.—$[\{CuL(CH_3COO)\}_2]$. To a solution of 2-formylpyridine thiosemicarbazone (1.80 g, 10 mmol) in *NN*-dimethylformamide (70 cm^3) was added dropwise a solution of copper(II) acetate monohydrate (2.00 g, 10 mmol) in water (75 cm^3). The dark green microcrystalline precipitate was filtered off and washed with ethanol and diethyl ether. Yield 2.40 g (80%). Crystals were obtained by gently heating the complex (0.30 g) dissolved in water (80 cm^3) to 70 °C, filtering and allowing slow evaporation of the filtrate over a period of two weeks.

$[(CuLCl)_2]$. To a solution of 2-formylpyridine thiosemicarbazone (0.45 g, 2.5 mmol) in *NN*-dimethylformamide (20 cm^3) was added a solution of copper(II) chloride dihydrate (0.43 g, 2.5 mmol) in water (20 cm^3). The resulting yellow-green precipitate was washed with ethanol. Yield 0.50 g (72%).

$[(CuLX)_2]$ (X = Br *or* I). To 2-formylpyridine thiosemicarbazone (0.90 g, 5 mmol) dissolved in *NN*-dimethylformamide (35 cm^3) was added a solution of KBr (11.9 g, 100 mmol) or KI (16.6 g, 100 mmol) in water (50 cm^3). To the filtered solution was added copper(II) acetate monohydrate (1.0 g, 5 mmol) dissolved in water (40 cm^3). The brown precipitates were collected and washed with water and methanol. Yields: $[(CuLBr)_2]$, 1.33 g (82%); $[(CuLI)_2]$, 1.60 g (87%).

$[(CuLX)_2]$ (X = ClO_4 *or* NO_3). The ligand 2-formylpyridine thiosemicarbazone (1.80 g, 10 mmol) was dissolved in a solution of methanol (100 cm^3) and water (40 cm^3) with gentle heating. To this solution was added copper(II) perchlorate hexahydrate (3.70 g, 10 mmol) or copper(II) nitrate trihydrate (2.42 g, 10

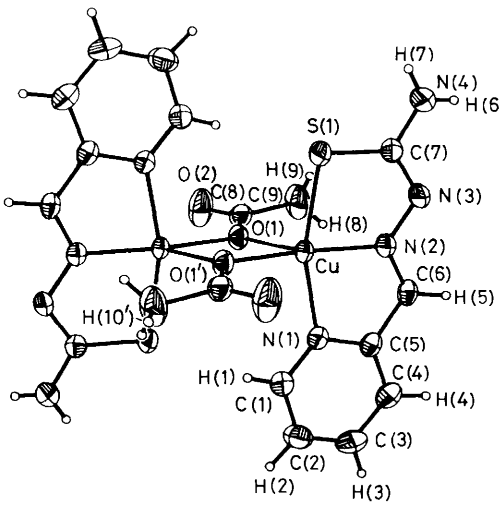

Figure 1. Structure of $[\{CuL(CH_3COO)\}_2]$

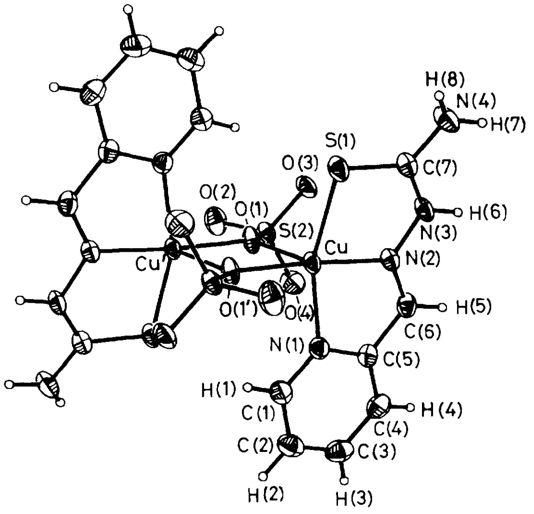

Figure 2. Structure of $[\{Cu(HL)(SO_4)\}_2]$

mmol) dissolved in water (40 cm^3) and the resulting green solution was filtered. A brown microcrystalline product appeared after 1—2 d; it was washed with methanol. Yields: $[\{CuL(ClO_4)\}_2]$, 1.60 g (47%); $[\{CuL(NO_3)\}_2]$, 0.55 g (18%).

$[\{Cu(HL)(SO_4)\}_2]$. Following the method of Hemmerich *et al.*,[14] a solution of $[\{CuL(CH_3COO)\}_2]$ (0.30 g) was heated to boiling in 2 mol dm^{-3} H_2SO_4 (30 cm^3) and the solution filtered. Large blue-green crystals appeared from the filtrate within 1—3 d. Yield 0.15 g (44%).

$[\{Cu(HL)Cl_2\}_2]\cdot 2H_2O$. The complex $[\{CuL(CH_3COO)\}_2]$ (0.32 g) was suspended in 4 mol dm^{-3} HCl (30 cm^3) and heated to 80 °C with stirring for 5 min. The resulting green precipitate was filtered off and washed with acetone. Yield 0.32 g (89%).

Results and Discussion

The complexes $[(CuLX)_2]$ were prepared by the reaction of the ligand HL with the appropriate copper salt in a 1:1 ratio (X = CH_3COO, Cl, ClO_4, or NO_3) or by reaction of an HL–KX mixture with copper(II) acetate monohydrate (X = Br or I). Dissolution of the complex $[\{CuL(CH_3COO)\}_2]$ in H_2SO_4 or HCl resulted in protonation of the ligand L with complexes of the type $[\{Cu(HL)(SO_4)\}_2]$ or $[\{Cu(HL)Cl_2\}_2]\cdot 2H_2O$ respectively being formed. Analytical data are given in Table 1 and while dimeric structures are assumed for all solid complexes by analogy to the structures of those characterised by *X*-ray crystallography (see below), further structural work is required to confirm this.

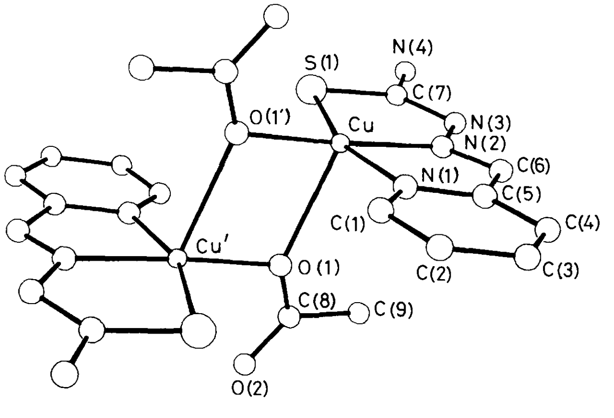

Figure 3. Parallel 2-formylpyridine thiosemicarbazone rings and staggered bridging acetate ions in $[\{CuL(CH_3COO)\}_2]$

Crystal Structures of Di-μ-acetato-bis[(*2-formylpyridine thiosemicarbazonato*)*copper*(II)], $[\{CuL(CH_3COO)\}_2]$, *and Di-μ-sulphato-bis*[(*2-formylpyridine thiosemicarbazone*)*copper*(II)], $[\{Cu(HL)(SO_4)\}_2]$.—Thermal ellipsoid drawings of the two structures, including the atom numbering scheme used, are depicted in Figures 1 and 2. Bond lengths and angles are given in Table 4. Both the complexes, $[\{CuL(CH_3COO)\}_2]$ and $[\{Cu(HL)(SO_4)\}_2]$, crystallize as discrete centrosymmetric dimers bridged by two acetato ligands in the former and two sulphato ligands in the latter. The co-ordination environment around the copper(II) atoms in each structure is similar and is shown more clearly for the acetato complex in Figure 3. This figure also illustrates two other structural features of the compounds, *viz.* the fact that the 2-formylpyridine thiosemicarbazone rings are parallel (due to the crystallographic centre of symmetry), but not in the same plane, and the staggered nature of the bridging acetate ions with the differing Cu–O bond distances [Cu–O(1') 1.951(1) and Cu–O(1) 2.427(2) Å].

The one-atom acetate bridging observed in the present work is uncommon, although it has been seen previously in at least two cases.[16,17] The normal mode of acetate bridging is *via* the two different acetate oxygen atoms to form a three-atom bridge,[16] as for example in copper(II) acetate monohydrate.[18] In line with the one-atom bridging mode the C(8)–O distances in the acetate ion are different, with the carbon to (co-ordinated) oxygen bond being the longer [C(8)–O(1) 1.279(3), C(8)–O(2) 1.224(4) Å]. Similarly the sulphate ions in $[\{Cu(HL)(SO_4)\}_2]$ also exhibit an unusual one-atom bridging mode which is reflected in the different S(2)–O bond lengths of 1.515(2) Å (co-ordinated oxygen) and 1.461(2) Å (mean value, unco-ordinated oxygens).

In both complexes, the copper atoms lie in an approximate plane of four co-ordinating atoms three of which come from the 2-formylpyridine thiosemicarbazone ligand (L or HL). The fourth co-ordination site is furnished by one oxygen from either an acetate or sulphate ion. The co-ordination sphere is completed by a less strongly bound oxygen from the second bridging ion. This gives rise to a distorted square-pyramidal geometry about the copper(II) atoms. Such an assignment to the geometry is supported by consideration of the copper–ligand bond angles (Table 4) and least-squares plane calculations

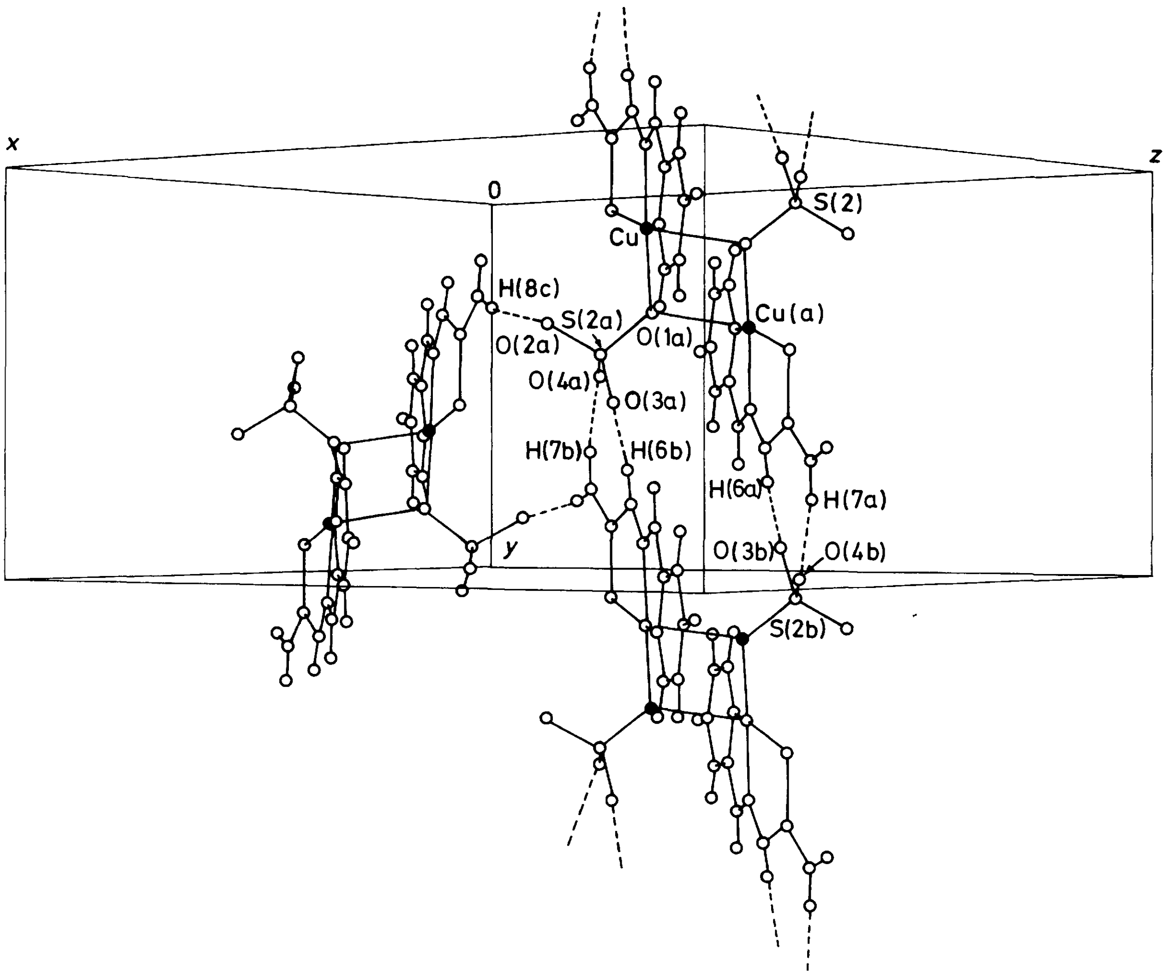

Figure 4. The hydrogen-bonding scheme in $[\{Cu(HL)(SO_4)\}_2]$. The symmetry transformations are: (a) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (b) $x, 1 + y, z$; (c) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. Bond lengths: H(6a)–O(3b) 1.82, H(7a)–O(4b) 1.93, H(8c)–O(2a) 2.20 Å; bond angles: N(3a)–H(6a)–O(3b) 167, N(4a)–H(7a)–O(4b) 169, N(4c)–H(8c)–O(2a) 164°

involving the five basal atoms Cu, S(1), N(1),N(2), and O(1′). In $[\{CuL(CH_3COO)\}_2]$, the copper sits out of the mean plane (displacement 0.086 Å) to a greater extent than the other co-ordinated atoms [S(1) −0.042, N(1) −0.047, N(2) 0.008, and O(1′) −0.005 Å]. In $[\{Cu(HL)(SO_4)\}_2]$ the distortion of the basal plane is more severe, the following displacements from the mean being observed: Cu −0.093, S(1) 0.138, N(1) 0.165, N(2) −0.126, and O(1′) −0.084 Å. Finally it should be noted that there is a weak sixth contact between the bridging ligands and the copper atoms (Cu′–O(2) 3.128(2) Å for $[\{CuL(CH_3COO)\}_2]$ and 2.925(2) Å for $[\{Cu(HL)(SO_4)\}_2]$) but this is not considered to be significant.

Despite the similarity of the co-ordination sphere around the copper atom in both complexes the crystal structures show that the 2-formylpyridine thiosemicarbazone ligand exists in the deprotonated anionic form, L, only in the acetate complex, $[\{CuL(CH_3COO)\}_2]$. As mentioned in the introduction, the sulphate complex $[\{Cu(HL)(SO_4)\}_2]$ was originally formulated to contain hydrogensulphate ions,[14] implying the deprotonation of HL; however the location of the hydrogen atoms in both structures shows the 'additional hydrogen' in the sulphate complex to be bound to the N(3) atom. Both the good crystal quality and the low *R* values obtained add weight to the detection or non-detection of a hydrogen bound to N(3).

This hydrogen, H(6), is intermolecularly hydrogen-bonded to a sulphate oxygen, O(3), of an adjacent molecule and H(7) similarly interacts with O(4) of the same sulphate anion (see Figure 4). These interactions are part of an overall hydrogen-bonding scheme which generates chains of molecules parallel to the *b* axis. There are also weaker interactions between the chains involving H(8) and O(2) of a different sulphate. The result is that all the non-co-ordinated sulphate oxygens are involved in hydrogen-bonding interactions (albeit weakly in the latter case) suggesting that such interactions may be important in stabilising the neutral 2-formylpyridine thiosemicarbazone ligand complex $[\{Cu(HL)(SO_4)\}_2]$ in the solid state. In contrast, the acetate anion in the complex $[\{CuL(CH_3COO)\}_2]$ is not involved in hydrogen bonding. However the distance of 2.27 Å between the deprotonated nitrogen, N(3), and H(6a) of an adjacent molecule does suggest a weak intermolecular contact [N(3)–H(6a)–N(4a) 173°].

Further support for the structural characterization of both neutral and deprotonated ligand types comes from a consideration of the geometry of the 2-formylpyridine thiosemicarbazone itself in each complex. (i) Both the important resonance structures of HL point to N(3)–C(7) being longer than in the anionic form, L, and indeed this is found with the bond distances being 1.362(3) Å in $[\{Cu(HL)(SO_4)\}_2]$ *versus* 1.335(3) Å in $[\{CuL(CH_3COO)\}_2]$. (ii) Significant differences in bond lengths are also observed for the N(4)–C(7) bonds. The shorter N(4)–C(7) bond in $[\{Cu(HL)(SO_4)\}_2]$ 1.309(3) Å compared with 1.333(4) Å in $[\{CuL(CH_3COO)\}_2]$ can be attributed to the importance of the resonance structure HL(b). (iii) The fact that the C(7)–S(1) bond [1.725(2) Å] in $[\{CuL(CH_3COO)\}_2]$ is significantly longer than the C(7)–S(1) bond distance in $[\{Cu(HL)(SO_4)\}_2]$ [1.703(3) Å] is consistent with the increased single-bond character expected in the deprotonated form, L. {Similar longer C–S bond lengths of 1.724(8) and 1.739(8) Å have been observed in the structure of $[NiL_2]$[19] where the ligand is also anionic. In contrast, the crystal structures of the related free ligand, 5-hydroxy-2-formylpyridine thiosemicarbazone,[20] and of $[Cu(tsc)_2(NO_3)_2]$ (tsc = thiosemicarbazide),[21] where the thione tautomers [*e.g.* of the type HL(a)] will contribute, show shorter C–S bonds of 1.706(6) and 1.713(5) Å respectively.}

Considering the copper–ligand distances in the two complexes, the Cu–S bond lengths at 2.274(1) and 2.279(1) Å are only slightly different. Available literature evidence also indicates a lack of discrimination of the two types of sulphur in copper(II) complexes of thiosemicarbazides and thiosemicarbazones. Thus for compounds containing a thiolato-type sulphur, values of 2.263(1) and 2.267(1) Å were reported for the Cu–S bond in [Cu(kts)] [H_2kts = 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone)][22] and 2.234(3) and 2.237(3) Å for [benzil bis(thiosemicarbazonato)]copper (II).[23] Those involving formal thione sulphurs show values of 2.259(3) and 2.266(3) Å in $[Cu(tsc)_2(SO_4)]$[24] and 2.286(4) Å in $[Cu(tsc)_2(NO_3)_2]$.[21] Such factors as the steric requirements of the ligands and the geometry of the copper co-ordination sphere seem to override any differences in the electronic nature of the sulphur donor atoms. Moreover, electron delocalization is considered important in thiosemicarbazones, especially those containing aryl groups,[20,25] and this is demonstrated in the electronic flexibility of the co-ordinated 2-formylpyridine thiosemicarbazone anion, L in $[\{CuL(CH_3COO)\}_2]$, in accommodating the positive charge on going to HL, in $[\{Cu(HL)(SO_4)\}_2]$, without significantly altering its ligating properties.

Physicochemical Studies.—Enhancement of some Raman bands was observed for solid samples of $[(CuLX)_2]$ (X = CH_3COO or Cl) and $[\{Cu(HL)(SO_4)\}_2]$* when excited with a laser line of wavelength 676.4 nm which coincides with a region of visible absorbance for the complexes. Enhanced bands may be inferred to result primarily from vibrations involving the copper and adjacent donor atoms; however we prefer not to make assignments, although others have attempted to do so on similar compounds.[26–32]

The occurrence of two bands at 1 175 and 1 020 cm^{-1} (corresponding to ν_3 of the free sulphate ion) in the i.r. spectrum of $[\{Cu(HL)(SO_4)\}_2]$ and additional bands at 612 and 598 cm^{-1} (ν_4 state in the free dianion) suggests that the sulphate ligands have local C_{3v} symmetry[33] as proven by the crystallographic study. Another band due to ν(SO) appears at 942 cm^{-1}.

The reflectance spectra for the complexes are reported in Table 1. In general two absorption maxima are observed. In all cases the band in the range 640—725 nm is assigned to a predominantly *d–d* transition[34] and the second band, in the region 360—427 nm, to a charge-transfer transition. The former is consistent with the '4 + 1' co-ordination as found from the *X*-ray crystallography, with the strong in-plane interactions giving spectra reminiscent of square-planar co-ordinated copper. There appears to be a sequential drop in energy of the charge-transfer transition on going from the chloro to the iodo complexes. These transitions may therefore include both $X \rightarrow Cu^{II}$ (X = Cl, Br, or I) and $S \rightarrow Cu^{II}$ charge transfer-components.[34]

In aqueous solution, all the compounds dissolve to give green solutions which have corresponding bands at 385 and 630 nm ($\varepsilon \sim 200$ dm^3 mol^{-1} cm^{-1}). In the less polar solvent, dimethyl sulphoxide, the charge-transfer band moves to lower energy (to 415 nm) whereas the *d–d* band position is virtually unchanged. E.s.r. spectra in dimethyl sulphoxide are also all the same (see below). These results suggest that the complexes are decomposed in water and a mononuclear species of the type $[CuL(H_2O)]^+$ is formed. This is supported by conductivity measurements which showed $[(CuLCl)_2]$ to be a 1 : 1 electrolyte in water and $[\{CuL(CH_3COO)\}_2]$ to be a little less than a 1 : 1 electrolyte. The complex $[\{Cu(HL)(SO_4)\}_2]$ acts as a strong acid in water with a proton being removed from the ligand HL. In addition, conductivity studies indicate decomposition according to the equation below. Hence the common species in water for all these complexes is $[CuL(H_2O)]^+$ as has been stated previously for the acetato complex.[10]

$$\tfrac{1}{2}[\{Cu(HL)(SO_4)\}_2] \xrightarrow{H_2O} [CuL(H_2O)]^+ + H^+ + SO_4{}^{2-}$$

The magnetic moments for the complexes are listed in Table 1, and apart from $[(CuLX)_2]$ (X = NO_3 or ClO_4), which require further structural studies, they have normal spin-only values at room temperature.

The powder e.s.r. spectra of $[\{CuL(CH_3COO)\}_2]$, $[(CuLCl)_2]$, and $[\{Cu(HL)(SO_4)\}_2]$ at room temperature and 110 K each displayed three *g* values; these for $[\{CuL(CH_3COO)\}_2]$ are 2.20, 2.06, and 2.04, consistent with the rhombic symmetry of the copper sites. In frozen dimethyl sulphoxide solution the spectra are all of the same type, *e.g.* for $[\{CuL(CH_3COO)\}_2]$ $g_{\parallel} = 2.198$, $A_{\parallel} = 191 \times 10^{-4}$ cm^{-1}, and $g_{\perp} = 2.071$, in line with dimer dissociation in solution as mentioned above.

Conclusions

In 2-formylpyridine thiosemicarbazone complexes of copper(II) in the solid state, copper(II) is stabilized relative to copper(I). This is exemplified by the isolation of the iodo complex, $[(CuLI)_2]$. The presence of the tricyclic ring system from the 2-formylpyridine thiosemicarbazone ligand gives a rigid planar structure around the copper which contributes to the stability of the copper(II) state. Also, the electron-withdrawing effects of the aryl ring may have an influence.[25] In solution both $[\{CuL(CH_3COO)\}_2]$ and $[\{Cu(HL)(SO_4)\}_2]$ break up into $[CuL(solvent)]^+$ species. To rationalize the role of metal–thiosemicarbazone complexes in the pharmacological field further work needs to be applied to the reactions of such species in solution. This will be the subject of a later paper.

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* For $[\{CuL(CH_3COO)\}_2]$, 491, 446, 354, 312, 272, and 187 cm^{-1}; for $[(CuLCl)_2]$, 489, 353, 309, 216, and 166 cm^{-1}; for $[\{Cu(HL)(SO_4)\}_2]$, 506, 459, 420, 360, and 245 cm^{-1}.

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