Preparation and Characterization of Complexes of the Antitumour Copper(II) 2-Formylpyridine Thiosemicarbazone (HL) System and the Single-crystal X-Ray Structures of $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ and $[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$ *

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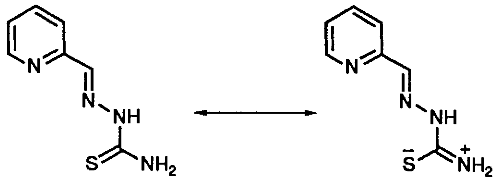
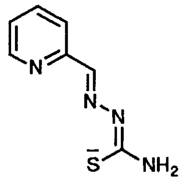
The complexes $[\{Cu(HL)X\}_2]X_2\cdot nH_2O$ (HL = 2-formylpyridine thiosemicarbazone, X = CF_3CO_2, F or I, $n = 0$; X = Br, $n = 2$) and $[Cu(HL)(H_2O)X_2]\cdot nH_2O$ (X = ClO_4, $n = 2$; X = NO_3, $n = 0$) have been prepared from the reaction of $[\{CuL(MeCO_2)\}_2]$ with the appropriate acid, HX. Also prepared were the deprotonated ligand complexes $[(CuLX)_2]\cdot nH_2O$ from the reaction of NaL with the appropriate copper(II) salt (X = F, $n = 5.5$; X = $\frac{1}{2}SO_4$, $n = 3$) or by the reaction of $[\{CuL(MeCO_2)\}_2]$ with the appropriate sodium salt, NaX (X = N_3, $n = 1$; X = CN, $n = 2$). The complexes have been characterized by a variety of physicochemical techniques and the crystal and molecular structures of $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ and $[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$ determined by single-crystal X-ray diffraction studies. Crystals of $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ are triclinic, space group $P\bar{1}$, with a = 9.6015(7), b = 10.837(1), c = 8.811(2) Å, α = 100.71(1), β = 117.06(1), γ = 80.877(7)°, and Z = 1. The complex cation is a centrosymmetric dimer, the monomeric units being bridged by two $CF_3CO_2^-$ anions. The copper atoms have a distorted square-pyramidal co-ordination geometry with three donor atoms (NNS) coming from HL and the fourth donor (an oxygen) from the bridging anion. The fifth position is occupied by a less strongly bound oxygen from the second bridging anion. Crystals of $[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$ are monoclinic, space group $P2_1/c$, with a = 12.9615(5), b = 9.7638(4), c = 14.9964(8) Å, β = 111.580(4)°, and Z = 4. The complex is monomeric with a distorted tetragonal co-ordination around the copper atom. The four in-plane donor atoms are provided by HL (NNS) and an oxygen from a co-ordinated water molecule. Two weakly bound ClO_4^- ions occupy the fifth and sixth positions. In both complexes hydrogen-bonding schemes appear to be important in stabilizing them in the solid state. The differences in the bonding parameters for the $Cu(HL)^{2+}$ and CuL^+ systems are discussed and related to the fact that the $S \rightarrow Cu^{II}$ ligand-to-metal charge-transfer absorption (at *ca.* 400 nm) is always observed at higher energies for the HL complexes.

Interest in copper(II) 2-formylpyridine thiosemicarbazone (HL) complexes arises from the marked antitumour properties of the compound $[\{CuL(MeCO_2)\}_2]$,[1] only recently characterized as a dimer in the solid state by single-crystal X-ray crystallography.[2,3] The deprotonated ligand L co-ordinates as a planar NNS tridentate group, which generates a tricyclic ligating system with the sulphur donor being formally of the thiolato-type. In an attempt to understand more fully the mode of action of the drug we are exploring the chemistry of the Cu^{II}–HL system. In a previous paper[4] we reported that the CuL^+ moiety forms Lewis-base adducts with a range of N and S donor ligands, *e.g.* $[CuL(bipy)]ClO_4$ (bipy = 2,2′-bipyridyl), thus substantiating the feasibility of adduct formation as a step in the proposed mechanism of action.[1] The stability and electronic flexibility of CuL^+ is demonstrated by the isolation of neutral ligand (HL) complexes from aqueous solutions at low pH. For example we showed that in the complex $[\{Cu(HL)(SO_4)\}_2]$ the ligand still co-ordinates as a planar NNS tridentate entity but the sulphur atom is now a thione-type, protonation having occurred on a chelate-ring nitrogen.[2]



HL



L

In this paper we develop the chemistry of the neutral ligand (HL) complexes with copper(II) and report the single-crystal X-ray structures of the complexes $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ and $[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$. The isolation and characterization of the latter compound is important since it supports conclusions from solution studies that suggest $[CuL(H_2O)]^+$ is the active species *in vivo*.[2,5,6] We also report

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* Di-μ-trifluoroacetato-κ*O*-bis[(2-formylpyridine-κ*N* thiosemicarbazone-$\kappa^2 N',S$)copper(II) bis(trifluoroacetate) and aqua-2-formylpyridine-κ*N* thiosemicarbazone-$\kappa^2 N',S$)diperchlorato-$\kappa^2 O$-copper(II) dihydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Colours, analytical and magnetic data for the complexes

		Analysis (%)[a]			
Complex	Colour	C	H	N	μ_{eff}[b]
$[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$	Green-black	28.2 (28.1)	1.7[c] (1.7)		1.83
$[\{Cu(HL)F\}_2]F_2$	Dark green	29.4 (29.8)	2.9 (2.9)	19.5[d] (19.9)	1.45
$[\{Cu(HL)Br\}_2]Br_2{\cdot}2H_2O$	Green	19.9 (19.9)	2.3 (2.4)	13.5 (13.3)	1.78
$[\{Cu(HL)I\}_2]I_2$	Red-orange	16.8 (16.9)	1.8 (1.6)	11.2[e] (11.3)	0.43
$[Cu(HL)(H_2O)(ClO_4)_2]{\cdot}2H_2O$	Emerald	17.6 (17.6)	2.3 (3.0)	11.6 (11.8)	1.87
$[Cu(HL)(H_2O)(NO_3)_2]$	Green	21.7 (21.8)	2.6 (2.6)	21.6 (21.8)	1.82
$[(CuLF)_2]{\cdot}5.5H_2O$	Dark green	27.1 (27.0)	3.3 (4.0)	17.4[f] (18.0)	1.71
$[(CuL)_2(SO_4)]{\cdot}3H_2O$	Green	26.2 (26.5)	2.5 (3.2)	17.6 (17.6)	1.76
$[\{CuL(N_3)\}_2]{\cdot}H_2O$	Dark green	28.6 (28.6)	2.4 (2.4)	34.2 (33.4)	1.83
$[\{CuL(CN)\}_2]{\cdot}2H_2O$	Brown	34.0 (33.5)	2.9 (3.2)	24.6 (24.2)	2.04

[a] Calculated values given in parentheses. [b] Measured at 293 K. [c] F, 24.3 (24.5%). [d] F, 13.4 (13.4%). [e] I, 50.9 (51.0%). [f] F, 6.4 (6.1%).

the synthesis and characterization of some new anionic L ligand complexes for the purpose of comparison.

Experimental

Microanalyses (Table 1), magnetic susceptibility, conductivity, IR, electronic and X-band ESR spectral measurements were carried out as described previously.[4] The ligand HL was synthesised following a published method[7] as were the complexes $[\{CuL(MeCO_2)\}_2]$, $[\{Cu(HL)Cl\}_2]Cl_2$, $[\{Cu(HL)(SO_4)\}_2]$ and $[(CuLX)_2]$ (X = Cl, Br, I, ClO_4 or NO_3).[2] All the complexes were dried under vacuum.

Preparation of the Copper Complexes.—$[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$. The complex $[\{CuL(MeCO_2)\}_2]$ (302 mg, 0.50 mmol) was dissolved in trifluoroacetic acid (2.6 mol dm^{-3}, 25 cm^3) with heating. The hot solution was filtered and allowed to stand for 1 d. The resulting crystals were washed with diethyl ether. Yield 182 mg (39%).

$[\{Cu(HL)F\}_2]F_2$, To a solution of HF (3 mol dm^{-3}, 7 cm^3), in a plastic beaker, was added the complex $[\{CuL(MeCO_2)\}_2]$ (260 mg, 0.43 mmol) with heating to form a saturated solution. Undissolved solids were removed by filtration and the solution allowed to stand for 6 weeks. The resulting solid was thoroughly dried *in vacuo*. Yield 175 mg (72%).

$[\{Cu(HL)X\}_2]X_2{\cdot}nH_2O$ (X = Br, n = 2; X = I, n = 0). The complex $[\{CuL(MeCO_2)\}_2]$ (320 mg, 0.53 mmol) dissolved in water (20 cm^3) was added to the appropriate concentrated acid HX (10 cm^3) and the mixture heated for 5 min. The resulting precipitates were washed with acetone. Yields: $[\{Cu(HL)Br\}_2]Br_2{\cdot}2H_2O$, 407 mg (91%); $[\{Cu(HL)I\}_2]I_2$, 483 mg (92%).

$[Cu(HL)(H_2O)X_2]{\cdot}nH_2O$ (X = ClO_4, n = 2; X = NO_3, n = 0). The complex $[\{CuL(MeCO_2)\}_2]$ (155 mg, 0.26 mmol) was dissolved in the appropriate acid HX (0.3 mol dm^{-3}, 10 cm^3) and the solution allowed to stand for several weeks. The resulting crystals were washed with the acid HX (0.3 mol dm^{-3}). Yields: $[Cu(HL)(H_2O)(ClO_4)_2]{\cdot}2H_2O$, 66 mg (28%); $[Cu(HL)(H_2O)(NO_3)_2]$, 127 mg (65%). **CAUTION**: the perchlorate complex may explode on gentle heating.

$[(CuLF)_2]{\cdot}5.5H_2O$. The compound $CuF_2{\cdot}2H_2O$ (282 mg, 2.05 mmol) was added slowly with stirring to a hot solution of the ligand HL (400 mg, 2.22 mmol) and Na (60 mg, 2.61 mol) in methanol (40 cm^3). The resulting solution was boiled for 5 min, filtered and reduced in volume to 20 cm^3 using a rotary evaporator. After 3 h at 0 °C the product separated out and was washed with diethyl ethr. Yield 264 mg (41%). It is hygroscopic.

$[(CuL)_2(SO_4)]{\cdot}3H_2O$. To a hot solution of HL (301 mg, 1.67 mmol) and Na (47 mg, 2.04 mmol) in ethanol (40 cm^3) was added $CuSO_4{\cdot}5H_2O$ (417 mg, 1.67 mmol) in water (10 cm^3). The resulting green precipitate was washed with water, ethanol and diethyl ether. Yield 288 mg (54%).

$[\{CuL(N_3)\}_2]{\cdot}H_2O$. To a solution of the complex copper(II) acetate monohydrate (322 mg, 1.66 mmol) in methanol (30 cm^3) was added NaN_3 (140 mg, 2.15 mmol) in water (10 cm^3) and HL (296 mg, 1.64 mmol) in methanol (30 cm^3). The resulting solution was heated under reflux for 1 h. The product was washed with water, methanol and diethyl ether. Yield 386 mg (79%).

$[\{CuL(CN)\}_2]{\cdot}2H_2O$. To a hot solution of the complex $[\{CuL(MeCO_2)\}_2]$ (302 mg, 1.00 mmol) in water (100 cm^3) was added dropwise NaCN (53 mg, 1.08 mmol) in the same solvent (10 cm^3). The resulting brown precipitate was washed with hot water. Yield 94 mg (33%).

Crystal Structure of Di-μ-trifluoroacetato-bis[(2-formylpyridine thiosemicarbazone)copper(II)] Bis(trifluoroacetate), $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$.—*Crystal data*. $C_{22}H_{16}Cu_2F_{12}N_8O_8S_2$, M = 939.6, triclinic, space group $P\bar{1}$, a = 9.6015(7), b = 10.837(1), c = 8.811(2) Å, α = 100.71(1), β = 117.06(1), γ = 80.877(7)°, U = 799.3 Å^3 (by least-squares refinement on the setting angles of 25 automatically centred reflections), λ = 1.5418 Å, Z = 1, D_c = 1.952 g cm^{-3}. Dark green crystals, dimensions 0.60 × 0.15 × 0.04 mm; crystal faces $\{1\,0\,0\}$, $\{0\,1\,0\}$, $\{0\,0\,1\}$, $\{\bar{1}\,0\,0\}$, $\{0\,\bar{1}\,0\}$, $\{0\,0\,\bar{1}\}$, μ(Cu-Kα) = 38.36 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω–2θ scan, with ω scan width = 0.8 + 0.14 tan θ, ω scan speed 0.78–5.49° min^{-1}, maximum count time 100 s, Cu-Kα radiation, 3504 reflections measured ($1 \leqslant \theta \leqslant 75°$, $\pm h$ $\pm k$ $+l$), 3176 unique [merging R = 0.016 after absorption correction (maximum, minimum transmission factors = 0.78, 0.23 respectively)] giving 2974 with $F > 3\sigma(F)$. Crystal decay of *ca.* 12.5% corrected during processing.

Structure analysis and refinement. The structure was solved by heavy-atom methods and refined by the full-matrix least-squares technique. A difference electron-density map revealed considerable disorder associated with the fluorine atoms in both trifluoroacetate anions (occupancy factors were estimated having regard to the overall isotropic thermal parameters for each set of sites). The six highest-occupancy fluorine positions for each anion and all other non-hydrogen atoms were refined assuming anisotropic thermal motion. Hydrogen atoms were included at calculated positions riding on the atom to which they were attached with one overall isotropic thermal parameter (U = 0.10 Å^2). The exceptions to this were H(41) and H(42) for which sites were identified on the difference map. Their parameters were then fixed. The weighting scheme, $w = 1/[\sigma^2(F_o) + 0.016\,744F_o^2]$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values are 0.070 and 0.082 respectively for the 347 parameters refined; $F(000) = 462$. Atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 4. The numbering system used is shown in Fig. 1. Initial data processing was performed using the Enraf-Nonius Structure Determining Package.[8] Least-squares refinement[8] was by means of program SHELX 76 adapted to allow refinement of up to 400 parameters. Atomic scattering factors were from the tabulations of Cromer and Mann[8] with anomalous dispersion corrections from Cromer and Liberman.[8]

Crystal Structure of Aqua(2-*formylpyridine thiosemicarbazone*)*diperchloratocopper*(II) *Dihydrate*, [Cu(HL)(H$_2$O)(ClO$_4$)$_2$]·2H$_2$O.—*Crystal data*. $C_7H_{14}Cl_2CuN_4O_{11}S$, M = 496.8, monoclinic, space group $P2_1/c$, a = 12.9615(5), b = 9.7638(4), c = 14.9964(8) Å, β = 111.580(4)°, U = 1764.2 Å^3 (by least-squares refinement on the setting angles of 25 automatically centred reflections), λ = 1.5418 Å, Z = 4, D_c = 1.87 g cm^{-3}. Emerald-green crystals, dimensions 0.45 × 0.25 × 0.20 mm, crystal faces $\{1\,1\,0\}$, $\{\bar{1}\,1\,0\}$, $\{0\,1\,1\}$, $\{1\,0\,1\}$, $\{\bar{1}\,\bar{1}\,0\}$, $\{1\,\bar{1}\,0\}$, $\{\bar{1}\,0\,1\}$, $\{0\,\bar{1}\,1\}$, $\{0\,1\,\bar{1}\}$, μ(Cu-Kα) = 62.8 cm^{-1}.

Data collection and processing. Instrument and settings as above. 3792 Reflections measured ($1 \leqslant \theta \leqslant 75°$, $+h$ $+k$ $\pm l$, 3629 unique [merging R = 0.036 after absorption correction (maximum, minimum transmittion factors = 0.38, 0.07 respectively)] giving 3247 with $F > 3\sigma(F)$. Crystal decay of *ca*. 4.8% corrected during processing.

Structure analysis and refinement. The structure was solved by heavy-atom methods and refined by the full-matrix least-squares technique. All hydrogen atoms were located, those on the pyriding ring and C(6) being fixed with C–H distances of 1.08 Å. A difference electron-density map revealed peaks within bonding distance of Cl(2) which were included as one-quarter-weighted oxygens. All atoms except hydrogen were refined assuming anisotropic thermal motion; the parameters for hydrogen were fixed at U = 0.10 Å^2. The weighting scheme, $w = 1/[\sigma^2(F_o) + 0.115\,193\ F_o^2]$ with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values are 0.059 and 0.072 respectively for the 263 parameters refined; $F(000) = 1000$. Atomic coordinates are given in Table 3 and selected bond lengths and angles in Table 5. The numbering system used is shown in Fig. 2. Programs used and sources of scattering factor data are given in ref. 8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

When the complex [{CuL(MeCO$_2$)}$_2$] is dissolved in the appropriate acid protonation of the ligand L occurs, allowing the isolation of the neutral ligand (HL) complex [equations (1) and (2)]. The remarkable stability of the complexes in low pH solutions is demonstrated by the use of 2–4 mol dm^{-3} acids in their preparation. However in the case of the oxidizing acids (HClO$_4$ and HNO$_3$) 0.3 mol dm^{-3} solution had to be used to prevent ligand oxidation and decomposition to Cu^{2+}(aq).

$$[\{CuL(MeCO_2)\}_2] + 4HX \longrightarrow [\{Cu(HL)X\}_2]X_2 + 2MeCO_2H \quad (1)$$

$$X = CF_3CO_2, F, Br \text{ or } I$$

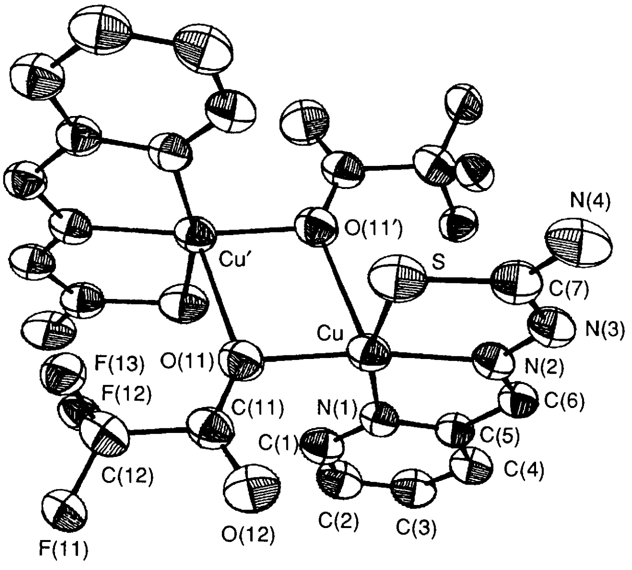

Fig. 1 The structure of the [{Cu(HL)(CF$_3$CO$_2$)}$_2$]$^{2+}$ cation showing the numbering system. Ellipsoids are drawn at the 50% probability level

$$[\{CuL(MeCO_2)\}_2] + 4HX + 2H_2O \longrightarrow 2[Cu(HL)(H_2O)X_2] + 2MeCO_2H \quad (2)$$

$$X = ClO_4 \text{ or } NO_3$$

We have not been able to prepare a neutral ligand (HL) complex from aqueous solution with acetate as co-anion, presumably because the acetate itself is protonated in preference to the co-ordinated L. Certainly the pK_a of acetic acid (4.75) is considerably higher than that of trifluoroacetic acid (−0.26) for example.[9] The anionic L ligand complexes, [(CuLX)$_2$], were prepared by its reaction with the parent copper(II) salt or by reaction of the sodium salt of the anion with [{CuL(MeCO$_2$)}$_2$] [equations (3) and (4)].

$$2CuX_2 + 2NaL \longrightarrow [(CuLX)_2] + 2NaX \quad (3)$$

$$X = F \text{ or } \tfrac{1}{2}SO_4$$

$$[\{CuL(MeCO_2)\}_2] + 2X^- \longrightarrow [(CuLX)_2] + 2MeCO_2^- \quad (4)$$

$$X = N_3 \text{ or } CN$$

Analytical (Table 1) and IR data indicate a number of the compounds should be formulated as hydrates. Where appropriate, IR data also confirm the presence of the co-anion [*e.g.* ν(CN) 2105, ν(N$_3$) 2060 cm^{-1}]. Dimeric structures are assumed for all the complexes in the solid, except the HL perchlorato and nitrato compounds, on the basis of the X-ray structural data presented below for [{Cu(HL)(CF$_3$CO$_2$)}$_2$][CF$_3$CO$_2$]$_2$ and previously[2] for [{CuL(MeCO$_2$)}$_2$] and [{Cu(HL)(SO$_4$)}$_2$]. The nitrato complex [Cu(HL)(H$_2$O)(NO$_3$)$_2$] is most likely a monomer, by analogy with the structure of the related perchlorate.

Crystal Structure of [{Cu(HL)(CF$_3$CO$_2$)}$_2$][CF$_3$CO$_2$]$_2$.—A thermal ellipsoid diagram for the cation of [{Cu(HL)(CF$_3$CO$_2$)}$_2$][CF$_3$CO$_2$]$_2$ is depicted in Fig. 1. Selected bond length and angle data are given in Table 4. The complex cation [{Cu(HL)(CF$_3$CO$_2$)}$_2$]$^{2+}$ is a centrosymmetric dimer bridged by two trifluoroacetato ligands. The remaining two trifluoroacetate anions are not co-ordinated. The co-ordination environment around the copper is a distorted square pyramid, the base consisting of the tridentate 2-formylpyridine thio-

Table 2 Fractional atomic coordinates (× 10^4) for [{Cu(HL)(CF_3CO_2)}$_2$][CF_3CO_2]$_2$ with standard deviations in parentheses *

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	5586.5(5)	4651.9(4)	2113.5(6)
S	8007(1)	3659(1)	2670(1)
F(11)	6961(33)	9046(16)	2260(32)
F(12)	5069(31)	8376(26)	83(55)
F(13)	7482(27)	7754(23)	697(20)
F(21)	1773(27)	1426(30)	1773(47)
F(22)	2084(78)	−624(42)	512(47)
F(23)	4074(39)	661(43)	2752(55)
O(11)	5713(3)	6051(3)	1076(4)
O(12)	6995(4)	7037(3)	3717(4)
O(21)	1329(4)	−54(4)	3737(5)
O(22)	3488(4)	−1222(3)	3854(5)
N(1)	3481(3)	5271(3)	2142(4)
N(2)	5468(3)	3409(3)	3388(4)
N(3)	6648(4)	2518(3)	4033(4)
N(4)	9066(4)	1669(4)	4363(6)
C(1)	2484(4)	6258(3)	1451(5)
C(2)	1055(5)	6524(4)	1517(6)
C(3)	627(4)	5759(4)	2294(6)
C(4)	1664(4)	4734(4)	3016(5)
C(5)	3061(4)	4528(3)	2910(4)
C(6)	4236(4)	3502(3)	3655(4)
C(7)	7897(4)	2531(4)	3735(5)
C(11)	6420(4)	6948(3)	2174(5)
C(12)	6500(5)	8049(4)	1315(5)
C(21)	2411(4)	−375(3)	3330(5)
C(22)	2436(5)	340(4)	2004(6)

* One set of disordered fluorine sites is given for each $CF_3CO_2^-$ anion.

Table 3 Fractional atomic coordinates (× 10^4) for [Cu(HL)(H_2O)(ClO_4)$_2$]·2H_2O with standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	2332.5(4)	746.3(4)	2456.0(3)
Cl(1)	5146(1)	668(1)	2384(1)
Cl(2)	−788(1)	1592(1)	1811(1)
S	3137(1)	−71(1)	3979(1)
O(1)	1906(2)	−991(3)	1803(2)
O(2)	2884(3)	−2053(3)	671(2)
O(3)	3826(3)	−161(4)	−243(3)
O(11)	4001(2)	1031(3)	1910(2)
O(12)	5807(3)	1464(4)	2002(3)
O(13)	5283(3)	−766(3)	2254(4)
O(14)	5458(3)	993(4)	3401(2)
O(21)	281(4)	1273(9)	2457(3)
O(22)	−1480(8)	1707(10)	2377(6)
O(23)	−1110(7)	291(7)	1307(5)
O(24)	−906(6)	2564(8)	1095(7)
O(25)	−261(11)	3015(16)	2033(13)
O(26)	−1037(14)	1500(23)	796(11)
O(27)	−1797(18)	1861(30)	1956(15)
N(2)	2660(2)	2536(2)	3045(2)
N(3)	3199(2)	2664(3)	4010(2)
N(4)	4018(3)	1605(3)	5445(3)
C(1)	1211(3)	1549(4)	367(2)
C(2)	856(3)	2499(5)	−386(2)
C(3)	987(3)	3867(5)	−175(3)
C(4)	1484(3)	4269(4)	772(3)
C(5)	1841(3)	3293(3)	1485(2)
N(1)	1709(2)	1925(3)	1274(2)
C(6)	2371(3)	3600(3)	2506(2)
C(7)	3478(3)	1493(3)	4517(2)

Table 4 Selected distances (Å) and angles (°) for [{Cu(HL)(CF_3CO_2)}$_2$][CF_3CO_2]$_2$ with standard deviations in parentheses *

Cu–N(1)	2.037(3)	N(3)–C(7)	1.342(4)
Cu–N(2)	1.953(3)	N(4)–C(7)	1.316(4)
Cu–S	2.273(1)	C(5)–C(6)	1.463(4)
Cu–O(11)	1.955(2)	C(11)–C(12)	1.555(4)
Cu–O(11′)	2.519(4)	Cu · · · Cu′	3.557(4)
S–C(7)	1.716(3)	C(21)–C(22)	1.527(6)
N(1)–C(1)	1.348(4)	O(11)–C(11)	1.266(4)
N(1)–C(5)	1.350(4)	O(12)–C(11)	1.203(5)
N(2)–N(3)	1.345(4)	O(21)–C(21)	1.228(4)
N(2)–C(6)	1.293(4)	O(22)–C(21)	1.244(4)
N(1)–Cu–N(2)	80.2(1)	C(7)–S–Cu	96.3(1)
N(1)–Cu–S	163.9(1)	Cu–O(11)–C(11)	113.2(2)
N(1)–Cu–O(11)	96.6(1)	Cu′–O(11)–C(11)	142.1(4)
N(1)–Cu–O(11′)	91.9(1)	C(4)–C(5)–C(6)	122.6(3)
N(2)–Cu–S	84.3(1)	N(1)–C(5)–C(6)	114.6(3)
N(2)–Cu–O(11)	172.9(1)	C(5)–C(6)–N(2)	114.9(3)
N(2)–Cu–O(11′)	111.0(1)	N(2)–N(3)–C(7)	116.1(3)
S–Cu–O(11)	98.4(1)	C(6)–N(2)–N(3)	120.8(3)
S–Cu–O(11′)	97.6(1)	N(3)–C(7)–S	121.6(2)
O(11)–Cu–O(11′)	75.2(1)	N(3)–C(7)–N(4)	116.9(3)
Cu–O(11)–Cu′	104.8(1)	S–C(7)–N(4)	121.4(3)
Cu–N(1)–C(1)	128.6(2)	O(11)–C(11)–O(12)	128.7(3)
Cu–N(1)–C(5)	112.5(2)	O(11)–C(11)–C(12)	112.2(3)
C(6)–N(2)–Cu	117.5(2)	O(12)–C(11)–C(12)	119.1(3)
N(3)–N(2)–Cu	121.6(2)		

* Atoms C(21), C(22), O(21) and O(22) refer to the non-co-ordinated $CF_3CO_2^-$ ion.

semicarbazone ligand which furnishes a NNS donor set, and the fourth position is occupied by an oxygen from the trifluoroacetate ion. The co-ordination sphere is completed by a fifth axial oxygen from a more weakly bound bridging $CF_3CO_2^-$ ion. Overall the structure of the cationic dimer is very similar to that of [{CuL($MeCO_2$)}$_2$][4] despite the fact that the thiosemicarbazone ligand is in the deprotonated form in this latter case. For instance in the trifluoroacetato complex the 'plane of best fit' through the basal donor atoms S,N(1),N(2) and O(11) shows the copper atom to be displaced out of the mean plane by 0.103 Å towards the bridging axial oxygen O(11′). For [{CuL($MeCO_2$)}$_2$] the analogous distance is only slightly less, being 0.086 Å. There is a weak sixth contact of the non-co-ordinated trifluoroacetate oxygen O(12) and the copper atom [Cu · · · O(12) 2.918(2) Å] but this is not considered significant although it effectively blocks the sixth position from approach by another ligand. Similar weak interactions were observed in the structures of [{CuL($MeCO_2$)}$_2$] and [{Cu(HL)(SO_4)}$_2$].[2]

The in-plane bond distances for [{Cu(HL)(CF_3CO_2)}$_2$]$^{2+}$ may be compared with the values for the acetate complex. The Cu–S and Cu–O distances at 2.273(1) and 1.955(2) Å are not significantly different from the values of 2.274(1) and 1.951(1) Å observed for the analogous bonds in the acetate. However, the Cu–N(1) and Cu–N(2) distances are shorter [2.037(3) *cf.* 2.059(2) Å and 1.953(3) *cf.* 1.970(2) Å respectively]. While it may be tempting to ascribe these differences to changes in the co-ordinated 2-formylpyridine thiosemicarbazone ligand on going from L to HL, a survey of eight different copper(II) complexes (including those reported in this paper) remarkably demonstrates that there are no differences between the *average* in-plane bond lengths when L is protonated.[2,4,10] The average values for the CuL$^+$ and Cu(HL)$^{2+}$ species are: Cu–N(1) 2.021(5) and 2.023(3); Cu–N(2) 1.952(6) and 1.953(3); Cu–S 2.276(2) and 2.279(1) Å respectively. The shorter Cu–N(1) and Cu–N(2) distances for the trifluoroacetato complex are compensated by a weaker axial interaction. The Cu–O(11′) distance for [{Cu(HL)(CF_3CO_2)}$_2$]$^{2+}$ is 2.519(4) Å compared with the value of 2.427(2) Å for the acetate.

The 2-formylpyridine thiosemicarbazone ligand (HL) is approximately planar, with the biggest deviation from the plane being 0.037 Å for N(2). Examination of the bond length data shows that all the distances in the side chain are intermediate between formal single and double bonds. Both facts point to extensive electron delocalization over the entire ligand.

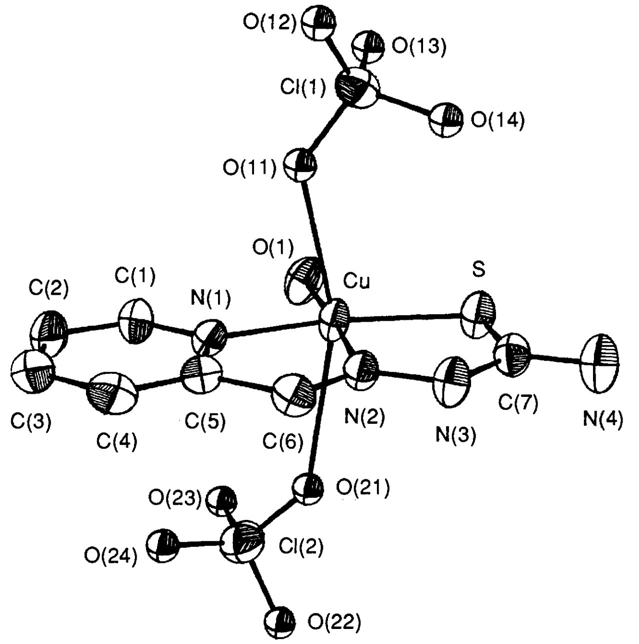

Fig. 2 The structure of the complex $[Cu(HL)(H_2O)(ClO_4)_2]$ showing the numbering system. Ellipsoids are drawn at the 50% probability level

Table 5 Selected distances (Å) and angles (°) for $[Cu(HL)(H_2O)(ClO_4)_2]{\cdot}2H_2O$ with standard deviations in parentheses

Cu–N(1)	2.016(3)	N(1)–C(1)	1.325(4)
Cu–N(2)	1.933(2)	N(1)–C(5)	1.369(4)
Cu–S	2.278(1)	N(2)–N(3)	1.363(4)
Cu–O(1)	1.935(2)	N(2)–C(6)	1.285(4)
Cu–O(11)	2.594(3)	N(3)–C(7)	1.346(4)
Cu–O(21)	2.710(5)	N(4)–C(7)	1.313(5)
S–C(7)	1.708(3)	C(5)–C(6)	1.459(5)
N(1)–Cu–N(2)	80.5(1)	Cu–N(1)–C(1)	129.1(2)
N(1)–Cu–S	165.7(1)	Cu–N(1)–C(5)	112.2(2)
N(1)–Cu–O(1)	96.2(1)	C(6)–N(2)–Cu	118.7(2)
N(1)–Cu–O(11)	76.9(1)	N(3)–N(2)–Cu	120.6(2)
N(1)–Cu–O(21)	79.4(1)	C(7)–S–Cu	95.9(1)
N(2)–Cu–S	85.2(1)	Cu–O(11)–Cl(1)	130.4(2)
N(2)–Cu–O(1)	175.9(1)	Cu–O(21)–Cl(2)	139.7(3)
N(2)–Cu–O(11)	88.8(1)	C(4)–C(5)–C(6)	124.4(3)
N(2)–Cu–O(21)	83.1(2)	N(1)–C(5)–C(6)	114.4(3)
S–Cu–O(1)	98.1(1)	C(5)–C(6)–N(2)	114.2(3)
S–Cu–O(11)	103.1(1)	N(2)–N(3)–C(7)	116.6(2)
S–Cu–O(21)	98.8(1)	C(6)–N(2)–N(3)	120.8(3)
O(1)–Cu–O(11)	92.9(1)	N(3)–C(7)–S	121.6(2)
O(1)–Cu–O(21)	93.9(2)	N(3)–C(7)–N(4)	117.1(3)
O(11)–Cu–O(21)	155.9(2)	S–C(7)–N(4)	121.3(3)

However a more detailed consideration of the side-chain bond lengths for this and other HL and L complexes substantiates our earlier conclusion (based on $[\{Cu(HL)(SO_4)\}_2]$ and $[\{CuL(MeCO_2)\}_2]$[2]) concerning the difference between the neutral and deprotonated ligands. Average bond length data for eight copper(II) complexes of HL and L[2,4,10] and $[NiL_2]$[11] show that: (*i*) C(7)–S and N(4)–C(7) are always shorter for co-ordinated HL [1.710(4) *cf.* 1.733(7) Å and 1.310(4) *cf.* 1.338(8) Å respectively] and (*ii*) N(3)–C(7) is always longer in the HL complexes [1.354(4) *cf.* 1.331(8) Å]. The data confirm the importance of the resonance structures for HL and L depicted above and show how the electronic flexibility of the thiosemicarbazone system allows it to gain or lose a positive charge without significantly altering its ligating properties.

The average bond lengths and angles for the $CF_3CO_2^-$ ions agree well with those reported in the literature.[12] The monoatomic bridging $CF_3CO_2^-$ ion shows two distinct C(11)–O distances with the carbon to co-ordinated oxygen being the longer [C(11)–O(11) 1.266(4) *cf.* C(11)–O(12) 1.203(5) Å]. In the non-co-ordinated ion the differences are less [1.228(4) and 1.244(4) Å]. The marginally longer distance for C(21)–O(22) may be attributed to a strong hydrogen bond with the hydrogen atom on N(3) [N(3)···O(22) 2.590 Å]. The remaining oxygen of the non-co-ordinated $CF_3CO_2^-$ anion also forms hydrogen bonds with the hydrogens on two different N(4) atoms [N(4)···O(21) 2.816, H(41)···O(21) 2.16 and N(4)···O(21′) 2.809, H(42)···O(21′) 1.86 Å].

Crystal Structure of $[Cu(HL)(H_2O)(ClO_4)_2]{\cdot}2H_2O$.—A thermal ellipsoid diagram for the complex $[Cu(HL)(H_2O)(ClO_4)_2]$ is depicted in Fig. 2 and selected bond length and angle data are given in Table 5. The complex crystallizes as a monomer with a distorted-tetragonal co-ordination sphere around the copper atom. Bond parameters for the neutral 2-formylpyridine thiosemicarbazone ligand are similar to those found in $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ and other HL complexes.[2,10]

The equatorial sites in the complex are occupied by a NNS donor set from the tridentate HL ligand and an oxygen from a co-ordinated water molecule. Two perchlorato ions occupy the fifth and sixth positions with long Cu–O distances [2.594(3) and 2.710(5) Å] typical of a number of bis(perchlorato) complexes of copper(II).[13–17] The significant off-axis deviation [O(11)–Cu–O(21) 155.9(2)°] compared with the value of ≈180° often observed for such weakly co-ordinated perchlorato groups may arise from crystal-packing forces. The copper lies slightly out of the plane of the equatorial donor atoms by 0.023 Å, being displaced towards the shorter of the two copper–perchlorate bonds.

The two non-co-ordinated water molecules are involved in a hydrogen-bonding scheme which links the monomers *via* the co-ordinated water, the perchlorate ions and the hydrogen atom on N(3). The hydrogens of the co-ordinated water molecule, $H_2O(1)$ form two strong hydrogen bonds, one to a non-co-ordinated ClO_4^- oxygen [O(1)···O(22) 2.714 Å] and another to a second water molecule [O(1)···O(2) 2.674 Å]. This latter water molecule $H_2O(2)$ is then involved in two more hydrogen bonds, one to a ClO_4^- oxygen [O(2)···O(14) 2.828 Å] and another to the other lattice water molecule $H_2O(3)$ [O(3)···O(2) 2.830 Å]. Atom O(3) is involved in a total of four hydrogen-bonding contacts. One of these is to the hydrogen on N(3) [N(3)···O(3) 2.682 Å]. Another, the O(3)···O(12) hydrogen-bond interaction, at a distance of 3.119 Å must be considered very weak (the sum of the relevant van der Waals radii is 3.04 Å[18]). The Cl(1) perchlorate ion has two very weak contacts with the hydrogens on N(4) [N(4)···O(11′) 3.192 Å and N(4)···O(14′) 3.004 Å]. It is of note that both the structures of the HL complexes described in this paper, and also that of $[\{Cu(HL)(SO_4)\}_2]$,[2] show the hydrogen on N(3) to be involved in a hydrogen-bonding scheme either with a co-ordinated anion (SO_4^{2-}), a non-co-ordinated anion ($CF_3CO_2^-$) or a lattice water molecule. Such interactions appear to be important in stabilizing the neutral 2-formlypyridine thiosemicarbazone ligand complexes in the solid state.

Physicochemical Studies.—Electronic spectral data for the complexes in the solid state are given in Table 6. In each case the spectrum is dominated by an intense band in the range 385–435 nm, which is assigned to a $S \rightarrow Cu^{II}$ ligand-to-metal charge transfer (l.m.c.t.) transition.[2] This absorption band may also include an $X \rightarrow Cu^{II}$ l.m.c.t. (X = Cl, Br or I) component for the halide complexes.[2,19,20] For instance the iodo complexes are red-orange due to the tailing of an $I \rightarrow Cu^{II}$ c.t. band through the visible region. Also included in the table are compounds prepared previously[2] thus allowing a comparison of seven pairs of complexes with the same anion, but with the 2-formylpyridine thiosemicarbazone ligand either in the neutral (HL) or deprotonated (L) form *e.g.* as in $[\{Cu(HL)Cl\}_2]Cl_2{\cdot}2H_2O$ and

Table 6 Electronic spectral and molar conductivity data for the complexes

	Absorption maxima (nm)^a		
Complex	S→Cu	d–d	Λ^b/ S cm^2 mol^{-1}
$[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$	420	597	52
$[\{CuL(MeCO_2)\}_2]$	433	630	0
$[\{Cu(HL)F\}_2]F_2$	390sh	*c*	4
$[(CuLF)_2]\cdot 5.5H_2O$	429	650	13
$[\{Cu(HL)Cl\}_2]Cl_2\cdot 2H_2O$	382	705	37
$[(CuLCl)_2]\cdot H_2O$	428	646	1
$[\{Cu(HL)Br\}_2]Br_2\cdot 2H_2O$	386	705	60
$[(CuLBr)_2]$	426	652	13
$[\{Cu(HL)I\}_2]I_2$	428	*c*	60
$[(CuLI)_2]$	431	650	35
$[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$	386	621	65
$[\{CuL(ClO_4)\}_2]$	392	*c*	28
$[Cu(HL)(H_2O)(NO_3)_2]$	400	670	67
$[\{CuL(NO_3)\}_2]$	406	*c*	33
$[\{Cu(HL)(SO_4)\}_2]$	403	708	20
$[(CuL)_2(SO_4)]\cdot 3H_2O$	429	630	—
$[\{CuL(N_3)\}_2]\cdot H_2O$	425	600	0
$[\{CuL(CN)\}_2]\cdot 2H_2O$	430	*c*	8

^{a} Nujol-mull transmittance spectra. ^{b} In Me_2SO, values given per monomeric unit. ^{c} Obscured by S→Cu c.t. absorption.

$[(CuLCl)_2]\cdot H_2O$. The inclusion of $[\{Cu(HL)(CF_3CO_2)\}_2]$-$CF_3CO_2]_2$ and $[\{CuL(MeCO_2)\}_2]$ gives another pair. In each case the l.m.c.t. band for the protonated ligand complex is at higher energy (shorter wavelength) than for the corresponding deprotonated ligand complex, with an average difference of 23 nm for the eight pairs of complexes. Although the co-ordination geometry may not be identical for each pair of compounds, their d–d spectra, with one band in the range 600–710 nm, all point to[21] a '4 + 1' square-pyramidal geometry, as found for $[\{CuL(MeCO_2)\}_2]$,[2] $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ and $[\{Cu(HL)(SO_4)\}_2]$[2] or a '4 + 2' tetragonal geometry, as in $[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$. The HL or L ligand is in an equatorial position with the sulphur atom being an in-plane donor. As discussed earlier, there is no significant difference in the average values for the metal–ligand bonds for Cu^{II}–HL and Cu^{II}–L moieties. This implies that the decrease in energy of the S→Cu^{II} l.m.c.t. band, when HL is deprotonated, is a response to the change in the double-bond character of the bonds S–C(7), N(3)–C(7) and N(4)–C(7), causing the sulphur atom to become more 'thiolate-like'. Changes in axial ligation could also influence the energy of the l.m.c.t. bands. Consideration of the structures of $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ and $[\{CuL(MeCO_2)\}_2]$ shows the apical Cu–O distance to be 0.093 Å shorter in the latter complex. This would be expected to increase the energy of a l.m.c.t. band if all other factors were constant[22] but in fact the opposite occurs, pointing to the changes in the electronic distribution in HL on deprotonation being the dominating effect.

The d–d bands are observed on the tail of the l.m.c.t. absorptions only for three pairs of complexes, with the same co-anion (*i.e.* X = Cl, Br or $\frac{1}{2}SO_4$), which means comparisons should be made with caution. However the HL complexes all show the d–d band at lower energy than for the analogous anionic L ligand complexes, *e.g.* 705 nm for $[\{Cu(HL)Cl\}_2]$-$Cl_2\cdot 2H_2O$ and 646 nm fior $[(CuLCl)_2]\cdot H_2O$, which is in line with the different natures of the sulphur-donor atoms with the thiolato type of sulphur being expected to have the greater co-ordinating ability.[23] The reversal of the order for the trifuoroacetate/acetate pair may be a reflection of the slight difference in Cu–N equatorial and Cu–O axial bond lengths.

The molar conductance values, in dimethyl sulphoxide, are also listed in Table 6. Values for the L complexes fall well below the range expected (50–70 S cm^2 mol^{-1}) for 1 : 1 electrolytes[24] in most cases thus indicating anion co-ordination in this solvent. A comparison of the ESR spectral data for $[\{CuL(MeCO_2)\}_2]$, $[\{CuL(NCS)\}_2]$ (synthesis reported in ref. 25) and $[\{CuL(CN)\}_2]$ in frozen EtOH–Me_2SO solution (Table 7) gives further evidence for anion co-ordination. In the $g_{\parallel}$ region nitrogen superhyperfine lines are clearly seen, especially on the lowest field $M_I = \frac{3}{2}$ line. In the first example five lines are apparent, indicating two nitrogens coupled to the copper which are assumed to come from the L ligand donor set. For the last two complexes seven lines are discernible indicating three nitrogen atoms co-ordinated to the copper atoms presumably *via* anion bridging. For the neutral HL ligand complexes higher values are found for the molar conductivities consistent with either proton or anion ionization, although the former is favoured in view of the results for the L complexes.

The magnetic moments for the complexes (Table 1) in general have normal spin-only values at room temperatures. The exceptions unfortunately have not been crystallized, but do require further study. The ESR spectra (Table 7) show typical axial or rhombic type signals[26] for the solid complexes and those formulated as dimers do not show a signal for the forbidden $\Delta M = 2$ transition. However a low-temperature study on $[\{CuL(MeCO_2)\}_2]$ shows the copper atoms to be only very weakly antiferromagnetically coupled.[10]

Conclusion

The isolation and characterization of a range of neutral ligand 2-formylpyridine thiosemicarbazone (HL) complexes of copper(II) from low pH aqueous solution demonstrates the remarkable stability of such compounds. Their stability arises from the rigid tricyclic ring system around the copper atom. Comparison of metal–ligand bond parameters for $Cu(HL)^{2+}$ and CuL^+ chromophores in a range of compounds shows that, on average, there are no significant differences, but extensive delocalization within the ligand itself allows its electronic distribution to alter in response to charge differences arising from proton gain or loss. This is reflected in the higher-energy S→Cu^{II} l.m.c.t. transitions observed for the HL ligand complexes when compared with their anionic L analogues. While we have not yet obtained a crystalline complex containing deprotonated 2-formylpyridine thiosemicarbazone and a water molecule as the in-plane ligands, the structural characterization of the $[Cu(HL)(H_2O)]^{2+}$ species in the perchlorato complex supports the contention that [CuL-

Table 7 ESR spectral data for complexes

Complex	$g_\perp$	$g_\parallel$	$10^4 A_\parallel$/cm^{-1}	State
$[\{CuL(MeCO_2)\}_2]$	2.059	2.199	187[a]	*b*
$[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$	2.035 (g_1), 2.052 (g_2)	2.185 (g_3)		*c*
$[\{Cu(HL)F\}_2]F_2$	2.038	2.174		*c*
$[(CuLF)_2]\cdot 5.5H_2O$	2.074 (g_{iso})			*c*
$[\{Cu(HL)Br\}_2]Br_2\cdot 2H_2O$	2.045	2.176		*c*
$[\{Cu(HL)I\}_2]I_2$	2.061	2.227	174	*d*
$[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$	2.036 (g_1), 2.062 (g_2)	2.202 (g_3)		*c*
$[Cu(HL)(H_2O)(NO_3)_2]$	2.055	2.218		*c*
$[\{CuL(N_3)\}_2]\cdot H_2O$	2.053	2.178	181	*d*
$[\{CuL(NCS)\}_2]$	2.041 (g_1), 2.053 (g_2)	2.182 (g_3)		*c*
	2.055	2.190	184[e]	*b*
$[\{CuL(CN)\}_2]\cdot 2H_2O$	2.030	2.147		*c*
	2.045	2.151	183[e]	*b*

[a] $A_N \approx 13 \times 10^{-4}$ cm^{-1}. [b] In frozen EtOH–Me$_2$SO (9:1 v/v). [c] Powder. [d] In frozen Me$_2$SO. [e] $A_N \approx 11 \times 10^{-4}$ cm^{-1}.

$(H_2O)]^+$ (probably with weakly bound axial water molecules) is the active antitumour form of such systems *in vivo* at neutral pH.

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