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Chelating behaviour of methyl 2-pyridyl ketone carbono- and thiocarbono-hydrazones in copper(II) and zinc(II) complexes†

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The compounds bis(methyl 2-pyridyl ketone) carbono- (H_2L^1) and thiocarbono-hydrazone (H_2L^2) have been synthesized, their protonation constants obtained through spectrophotometric studies and their crystal structures determined by X-ray diffractometry. Their complexation behaviour has been studied towards copper and zinc chloride and acetate. The results indicate that they are able to form bimetallic complexes with both copper salts used and zinc acetate; this is confirmed by an X-ray analysis carried out on $[Cu_2(HL^1)Cl_3(OH_2)]\cdot1.5H_2O$.

During the last ten years a lot of work has been done with compounds that are able to co-ordinate to two or more metal atoms.[1] Materials chemistry, catalysis and bioinorganic chemistry are the areas mainly involved. Multinuclear complexes of transition-metal atoms have been proposed as molecular magnets,[2] active sites of metalloenzymes[3] or homogeneous catalysts.[4]

Continuing our work on the co-ordination chemistry of polydentate Schiff bases,[5] we have evaluated the possibility of obtaining multinuclear transition-metal complexes by using compounds obtained from the condensation of 2-acetylpyridine and carbono- or thiocarbono-hydrazide. The 2-acetylpyridine thiosemicarbazones are well known to have interesting biological activity (antitubercular, antitumour, antiviral, antifungal)[6] probably related to their chelating ability towards vital metal ions; moreover their complexes are inhibitors of the ribonucleotide diphosphate reductase enzyme.[7] Recently, also some 2-acetylpyridine thiocarbono-hydrazones have been found to show important antiviral activity,[8] but there is very little information about their co-ordination chemistry.[9]

With the aim of elucidating the co-ordination chemistry of this class of biologically important ligands, in the present paper we describe the synthesis and characterization of bis(methyl 2-pyridyl ketone) carbono- (H_2L^1) and thiocarbono-hydrazone (H_2L^2) and their copper and zinc complexes; the X-ray diffraction analysis of both proligands and of $[Cu_2(HL^1)Cl_3(OH_2)]\cdot1.5H_2O$ is also reported.

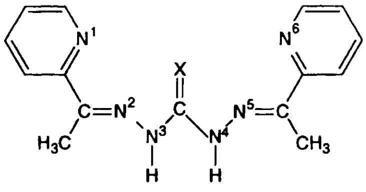
Experimental

Chemicals

All reagents were obtained commercially and used without subsequent purification.

Physical measurements

Elemental C, H and N analyses were carried out on a Carlo Erba Instruments CHNS-O EA1108 Elemental Analyser. Infrared spectra (4000–400 cm^{-1}) were recorded as KBr discs on a Nicolet 5PC FT-IR spectrometer, mass spectra with a Finnigan SSQ710 spectrometer and ^{1}H NMR spectra with a Bruker AC 300 instrument; chemical shift values are given in ppm referred to tetramethylsilane. The EPR spectrum at 298 K was obtained using a Varian E9 spectrometer operating at X-band frequency. Magnetic susceptibility measurements were performed on a powdered sample, in the temperature range 11.5–280 K, with an applied field of 1 T by using a Métronique Ingénierie MS03 SQUID magnetometer; the diamagnetic contribution to the susceptibility was estimated through Pascal's constants. Melting points were obtained with a Gallenkamp MFB-595 apparatus in open capillaries.



H_2L^1 X = O
H_2L^2 X = S

Spectrophotometric titrations

Each solution to be titrated was prepared in water–methanol (1 : 1, v/v), by subsequent addition of (1) a weighted amount of proligand (H_2L^1 or H_2L^2), (2) an exact volume of hydrochloric acid. pH Measurements were carried out with a fully automatic apparatus equipped with an Orion model 720A digital voltmeter and 5 cm^3 Metrohm E665 motor burette, both controlled by an Uvikon 941 PLUS spectrophotometer guided by a personal computer. The electrode combination consisted of a model OR (Orion Research) glass electrode (type 9101SC) and a model OR reference electrode (type 9002). In the cell the solution was thermostatted at 25.0 ± 0.1 °C and passed through the spectrophotometric cuvette using a peristaltic pump. The electrode system was calibrated in terms of pH by using five fresh buffers (pH 2.0, 4.0, 7.0, 9.0, 12.0). After each addition of KOH solution the pH was measured and the absorbance data in the range 210–500 nm were collected and recorded.

Calculations

The protonation constants for H_2L^1 and H_2L^2 were obtained by refinement of several sets of absorption data with the computer program SQUAD.[10] Typically the data contain the

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† *Non-SI units employed:* D ≈ 3.33 × 10^{-30} C m, G = 10^{-4} T, emu = SI × $10^6/4\pi$.

absorbance values, A_s, of a number of wavelengths for each of a number of equilibrium solutions of known analytical composition (pH and c_L). Assuming that Beer's law is valid, for each solution and wavelength the absorbance A_s is defined by equation (1) where ε_{pq} is the molar absorption coefficient for

$$A_{c,ik} = l\sum_{0}^{p}\sum_{0}^{q} \beta_{pq}[L]^p[H]^q\varepsilon_{pq} \tag{1}$$

the species H_qL_p and l is the cell pathlength, the sum being extended over all the free and complexed species assumed to be present in solution. For each solution the mass-balance equation (2) has to be solved at known pH for only protonation

$$c_l = [L] + \sum \beta_{pq}[L]^p[H]^q \tag{2}$$

equilibria. The unknown parameters in these equations are [L] (the free proligand ion concentration) for each solution, ε_{pq} at all the wavelengths and β_{pq} (the protonation constant). The values of [H] are obtained from potentiometric measurements. The sum of square errors, used in the refinement procedure, is defined as in equation (3), m = number of solutions and n =

$$U = \sum_{i=1}^{m}\sum_{k=1}^{n} |\Delta_{ik}|^2 = \sum_{ik}(A_{o,ik} - A_{c,ik})^2 \tag{3}$$

number of wavelengths, $A_{o,ik}$ and $A_{c,ik}$ are the observed and calculated absorbances at the ikth point, with i referring to the solution and k to the wavelength. In the program SQUAD, for each set of equilibrium constants β_{pq} to be varied, the concentrations of the various species in each solution are calculated, and then, for each wavelength and all solutions, the contribution to U for a systematically chosen number of sets of ε_{pq}. The first step, performed by the subroutine DIFF, is complete once the non-linear least-squares equations have been completely developed. The second step corresponds to the solution of the least-squares equations. Finally, in step three, a check is made to ensure that the current stability constants provide a better description of the data than that of the previous set.

X-Ray crystallography

Pertinent crystal data and basic information about the data collection and structure refinement are given in Table 2. The data were processed with the peak-profile analysis procedure and corrected for Lorentz-polarization and absorption effects.

The structures were solved by direct methods (SIR 92[11]) and refined by full-matrix least squares based on F^2. All non-hydrogen atoms were allowed anisotropic vibration, while the hydrogen atoms, which were in part located from difference maps and in part placed at idealized positions, were refined isotropically.

Calculations were performed on Gould POWER NODE 6040 and ENCORE91 computers using the SHELXL 92[12] program package. Other crystallographic programs used in the structure determination have been cited elsewhere.[13]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/70.

Preparations

Methyl 2-pyridyl ketone carbonohydrazone I. 2-Acetylpyridine (0.33 cm^3, 2.9 mmol) was added dropwise to a solution of carbonohydrazide (0.3 g, 3.3 mmol) in methanol (45 cm^3) with a few drops of acetic acid and refluxed for 6 h. On cooling a white solid precipitated. In all cases the purity was checked by TLC [Al_2O_3, ethyl acetate–CH_2Cl_2 (8:2) and a few drops of NEt_3]. Yield 75%, m.p. 202–203 °C (Found: C, 49.2; H, 5.4; N, 36.15. $C_8H_{11}N_5O$ requires C, 49.8; H, 5.7; N, 36.25%). Main IR bands: 3311m (br) [ν(NH_2)], 3200w (br) [ν(NH)], 3041w (br) [ν$(CH)_{aryl}$], 2980–2900w [ν$(CH)_{alkyl}$] and 1675vs cm^{-1} [ν(CO)]. UV (methanol): λ_{max} = 288 nm. Mass spectrum (chemical ionization, CI): m/z 194 (70, $[M + 1]^+$) and 162 {100%, $[(C_5H_4N)(CH_3)C{=}NNHCO]^+$}. $\delta_H[(CD_3)_2SO]$ 2.26 (3 H, s, CH_3), 4.14 (2 H, br, NH_2), 7.34 (1 H, t, py), 7.76 (1 H, t, py), 8.18 (1 H, br, NH), 8.38 (1 H, d, py), 8.52 (1 H, d, py) and 9.76 (1 H, br, NH).

Bis(methyl 2-pyridyl ketone) carbonohydrazone, H_2L^1. 2-Acetylpyridine (0.30 cm^3, 2.7 mmol) was added to carbonohydrazide (0.10 g, 1.1 mmol), dissolved in hot absolute ethanol (40 cm^3) with a few drops of glacial acetic acid. The solution was refluxed for 2 h and on cooling a white solid precipitated. It was recrystallized from absolute ethanol as colourless needles. Yield 70%, m.p. 186 °C (decomp.) (Found: C, 60.7; H, 5.8; N, 28.2. $C_{15}H_{16}N_6O$ requires C, 60.8; H, 5.4; N, 28.35%). Main IR bands: 3218m (br) [ν(NH)], 3050w (br) [ν$(CH)_{aryl}$], 2922–2853w [ν$(CH)_{alkyl}$] and 1696vs cm^{-1} [ν(CO)]. UV (methanol): λ_{max} = 299 nm. Mass spectrum (CI): m/z 297 (60, $[M + 1]^+$), 296 (20, M^+), 162 {100, $[(C_5H_4N)(CH_3)C{=}NNHCO]^+$} and 136 {90%, $[(C_5H_4N)(CH_3)C{=}NNH_3]^+$}. $\delta_H[(CD_3)_2SO]$ (peaks attributable to the main isomer) 2.38 (6 H, s, CH_3), 7.38 (2 H, t, py), 7.85 (2 H, t, py), 8.09 (2 H, d, py), 8.59 (2 H, d, py) and 10.30 (2 H, br, NH).

Methyl 2-pyridyl ketone thiocarbonohydrazone II. 2-Acetylpyridine (0.20 cm^3, 1.8 mmol) in methanol (70 cm^3) with a few drops of glacial acetic acid (0.20 cm^3), was added dropwise to thiocarbonohydrazide (0.18 g, 1.7 mmol) dissolved in methanol (30 cm^3). The solution was refluxed for 2 h. After evaporation of the solvent, white crystals of the product were obtained. Yield 80%, m.p. 153–154 °C (Found: C, 46.1; H, 5.65; N, 33.4; S, 15.55. $C_8H_{11}N_5S$ requires C, 45.9; H, 5.3; N, 33.5; S, 15.3%). Main IR bands: 3266s (br) [ν(NH_2)], 3166m (br) [ν(NH)], 3042w (br) [ν$(CH)_{aryl}$], 2951w (br), [ν$(CH)_{alkyl}$], 1578w [ν(C=C)] and 1505vs cm^{-1} (amide II). UV (methanol): λ_{max} = 310 nm. Mass spectrum (CI): m/z 210 (55, $[M + 1]^+$) and 178 {60%, $[(C_5H_4N)(CH_3)C{=}NNHCS]^+$} $\delta_H[(CD_3)_2SO]$ 2.36 (3 H, s, CH_3), 4.97 (2 H, br, NH_2), 7.36 (1 H, t, py), 7.78 (1 H, t, py), 8.50 (1 H, d, py), 8.57 (1 H, d, py), 9.93 (1 H, br, NH) and 10.27 (1 H, br, NH).

Bis(methyl 2-pyridyl ketone) thiocarbonohydrazone, H_2L^2. 2-Acetylpyridine (0.55 cm^3, 4.9 mmol) was added to thiocarbonohydrazide (0.21 g, 2 mmol), dissolved in hot absolute ethanol (40 cm^3) with a few drops of glacial acetic acid. The solution was refluxed for 5 h and on cooling a pale yellow solid precipitated. Crystals suitable for X-ray diffraction analysis were obtained from methanol. Yield 80%. m.p. 183–185 °C (lit.,[14] 160–162 °C) (Found: C, 57.5; H, 5.5; N, 27.1; S, 10.5. $C_{15}H_{16}N_6S$ requires C, 57.7; H, 5.2; N, 26.9; S, 10.3%). Main IR bands: 3201m (br) [ν(NH)], 3048w (br) [ν$(CH)_{aryl}$], 2922–2853w [ν$(CH)_{alkyl}$], 1586w [ν$(C{=}C)_{aryl}$], 1495vs [amide II + ν(C=N)] and 1294m cm^{-1} [ν(C–N) + ν(C=S)]. UV (methanol): λ_{max} = 325 nm. Mass spectrum (CI): m/z 312 (100%, M^-). $\delta_H[(CD_3)_2SO]$ (peaks attributable to the main isomer) 2.48 (6 H, s, CH_3), 7.43 (2 H, t, py), 7.89 (2 H, t, py), 8.19 (2 H, d, py), 8.62 (2 H, d, py) and 11.06 (2 H, br, NH).

$[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$. Compound H_2L^1 (0.06 g) was dissolved in hot absolute ethanol (40 cm^3) and $CuCl_2$ (0.06 g) was added. The solution was refluxed for 2 h. On cooling green crystals suitable for X-ray analysis separated. Yield 54%, m.p. ≈210 °C (decomp.) (Found: C, 31.3; H, 3.1; N, 14.1. $C_{15}H_{20}Cl_3Cu_2N_6O_{3.5}$ requires C, 31.4; H, 3.4; N, 14.65%).

Table 1 Cumulative and stepwise protonation constants of H_2L^1 and H_2L^2 at 25 °C

	H_2L^1	H_2L^2	$\Delta \log K^a$
$\log \beta_{11}$	13.40(1)	10.50(1)	
$\log \beta_{12}$	22.11(4)	17.27(5)	
$\log \beta_{13}$	26.29(4)	20.38(5)	
$\log \beta_{14}$	29.31(4)	22.74(5)	
$\log K_1^{\mathrm{H}\,b}$	13.40(1)^c	10.50(1)	2.90
$\log K_2^{\mathrm{H}}$	8.71(3)	6.77(4)	1.94
$\log K_3^{\mathrm{H}}$	4.18(4)	3.11(5)	1.07
$\log K_4^{\mathrm{H}}$	3.02(4)	2.36(5)	0.66
Z^d	3376	2482	
σ^e	5.0726×10^{-3}	6.0329×10^{-3}	
U^f	5.962×10^{-2}	6.362×10^{-2}	

[a] $\Delta \log K_n = \log K_n^{\mathrm{H}}(H_2L^1) - \log K_n^{\mathrm{H}}(H_2L^2)$. [b] $\log K_n = \log \beta_{1,n} - \log \beta_{1,n-1}$. [c] $\sigma(\log K_n) = \{[\sigma^2(\log \beta_{1,n}) + \sigma^2(\log \beta_{1,n-1})]/2\}^{\frac{1}{2}}$. [d] Total number of experimental data points used in the refinement. [e] $\sigma = \sum_{i=1} w_i(A_i^{\mathrm{obs}} - A_i^{\mathrm{calc}})^2/(Z - m)$, where m is the number of parameters to be refined. [f] Sum of squared residuals between observed and calculated absorbance (A).

Main IR bands: 3434m (br) [ν(NH), ν(OH)], 1636w [$\nu(C{=}C)_{aryl}$], 1590vs (amide II) and 1271m cm^{-1} (amide III).

$Cu_2(HL^1)(O_2CMe)_3$. The compound $Cu(O_2CMe)_2{\cdot}2H_2O$ (0.09 g) was added to H_2L^1 (0.06 g) previously dissolved in hot absolute ethanol (40 cm^3) and the green solution was refluxed for 2 h. The solvent was then removed and the product redissolved in MeCN; diethyl ether was added and a green microcrystalline powder precipitated. Yield 54%, m.p. ≈205 °C (decomp.) (Found: C, 41.4; H, 3.7; N, 14.5. $C_{21}H_{24}Cu_2N_6O_7$ requires C, 42.1; H, 4.0; N, 14.0%). Main IR bands: 3254m (br) [ν(NH)], 1593m [$\nu(C{=}C)_{aryl}$, amide II], 1371s [$\nu_{sym}(CO_2)$] and 1284m cm^{-1} (amide III).

$Zn(H_2L^1)Cl_2{\cdot}H_2O$. The compound H_2L^1 (0.06 g) was dissolved in hot absolute ethanol (40 cm^3); a yellow precipitate formed immediately after the addition of $ZnCl_2$ (0.06 g). The solution was refluxed for 1 h, then the powder was filtered off and washed with diethyl ether. Yield 57%, m.p. ≈277 °C (decomp.) (Found: C, 40.4; H, 4.2; N, 18.4. $C_{15}H_{18}Cl_2N_6O_2Zn$ requires C, 40.0; H, 4.0; N, 18.65%). Main IR bands: 3330 (br) [ν(NH), ν(OH)], 1688m [$\nu(C{=}O)$], 1616 (sh) [$\nu(C{=}C)_{aryl}$], 1596vs (amide II) and 1265m cm^{-1} (amide III).

$Zn_2(L^1)(O_2CMe)_2{\cdot}4.5H_2O$. The compound $Zn(O_2CMe)_2{\cdot}2H_2O$ (0.12 g) was added to H_2L^1 (0.08 g) previously dissolved in hot absolute ethanol (40 cm^3). The red solution was refluxed for 2 h, then the solvent was completely removed on a rotary evaporator and the crude product redissolved in the minimum volume of methanol. Addition of toluene gave a red precipitate which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 36%, m.p. ≈250 °C (decomp.) (Found: C, 37.0; H, 4.5; N, 13.3. $C_{19}H_{29}N_6O_{9.5}Zn_2$ requires C, 36.6; H, 4.65; N, 13.5%). Main IR bands: 3350 (br) [ν(OH)], 1616s [$\nu(C{=}C)_{aryl}$], 1576vs (amide II), 1358m [$\nu_{sym}(CO_2)$] and 1265m cm^{-1} (amide III).

$Cu(HL^2)Cl$. The compound H_2L^2 (0.05 g) was dissolved in hot absolute ethanol (40 cm^3), $CuCl_2{\cdot}2H_2O$ (0.02 g) was added. The green solution, refluxed for 2 h, gave a microcrystalline powder which was filtered off and dried *in vacuo*. Yield 53%, m.p. ≈250 °C (decomp.) (Found: C, 44.3; H, 4.1; N, 20.3; S, 7.8. $C_{15}H_{15}ClCuN_6S$ requires C, 43.9; H, 3.65; N, 20.5; S, 7.8%). Main IR bands: 3341m [ν(NH)], 1599w [$\nu(C{=}C)_{aryl}$] and 1515vs cm^{-1} (amide II).

$Cu_2(HL^2)Cl_3{\cdot}0.5EtOH$. The complex was prepared by a procedure similar to that described for $Cu(HL^2)Cl$, using $CuCl_2{\cdot}2H_2O$ (0.05 g). Yield 92%, m.p. ≈225 °C (decomp.) (Found: C, 33.8; H, 3.55; N, 14.7; S, 6.0. $C_{16}H_{18}Cl_3Cu_2N_6O_{0.5}S$ requires C, 33.9; H, 3.2; N, 14.8; S, 5.6%). Main IR bands: 3499 (br) [ν(OH), ν(NH)], 1606m [$\nu(C{=}C)_{aryl}$] and 1540vs cm^{-1} (amide II).

$Zn(HL^2)Cl{\cdot}EtOH{\cdot}H_2O$. The complex was prepared by a procedure similar to that described for $Cu(HL^2)Cl$, using $ZnCl_2$ (0.05 g): a yellow precipitate was immediately obtained. Yield 68%, m.p. ≈310 °C (decomp.) (Found: C, 42.8; H, 4.8; N, 17.9; S, 6.9. $C_{17}H_{23}ClN_6O_2SZn$ requires C, 42.9; H, 4.9; N, 17.65; S, 6.7%). Main IR bands: 3380 (br) [ν(OH)], 3209m [ν(NH)], 1615m [$\nu(C{=}C)_{aryl}$] and 1521vs cm^{-1} (amide II).

Reaction of H_2L^2 with $M(O_2CMe)_2{\cdot}2H_2O$ (M = Zn or Cu). In both reactions heterogeneous and not well characterized products were obtained probably owing to partial hydrolysis and decomposition of the ligand. In particular, when an ethanol solution of H_2L^2 was refluxed with $Zn(O_2CMe)_2{\cdot}2H_2O$ (2:1 metal to ligand ratio) for 2 h white crystals were isolated as the major product, which an X-ray diffraction analysis revealed to be Tatton's salt $[NH_4]_2[Zn(H_2O)_6][SO_4]_2$.

Results and Discussion

In solution the behaviour of the proligands is mainly determined by two factors: (1) the *E*-*Z* isomerism around the two imino double bonds and (2) the double-bond character of the central amide-type C–N bonds, so that there are many different conformers. On the NMR scale, at room temperature only one isomer of the mono derivatives of the carbono- and thiocarbono-hydrazide seems to be stable (for example, there is only one peak attributable to the methyl group at δ 2.36 for **II** and 2.26 for **I** respectively). On the contrary, the NMR spectra of H_2L^2 and H_2L^1 are very complex and greatly influenced by the temperature and solvent [methyl groups in H_2L^2 ($CDCl_3$) at 298 K; δ 2.45, 2.50, 2.52, 2.57, 2.58; at 323 K, 2.51, 2.47; [$(CD_3)_2SO$] at 298 K, 2.46, 2.48, 2.50; at 328 K, 2.47, 2.48, 2.50; at 360 K, 2.49]. The IR spectra of the proligands do not show any remarkable features; there are no bands attributable to the OH or SH of an hypothetical enolic or thioenolic form which, therefore, also on the basis of the X-ray results, can be excluded, at least in the solid state.

The mixed protonation constants obtained in this study are summarized in Table 1. The ligands have four protonation centres, the two hydrazonic nitrogens [N^3 and N^4, $\log K_1^{\mathrm{H}}$ = 13.40(1), $\log K_2^{\mathrm{H}}$ = 8.71(3) for H_2L^1 and 10.50(1), 6.77(4) for H_2L^2] and the two pyridine nitrogens [N^1 and N^6, $\log K_3^{\mathrm{H}}$ = 4.18(4), $\log K_4^{\mathrm{H}}$ = 3.02(4) for H_2L^1 and 3.11(5), 2.36(5) for H_2L^2]. All the overall and stepwise protonation constants of H_2L^1 are rather different from the corresponding ones of H_2L^2, where, in agreement with the literature findings, the presence of the sulfur atom increases the acidic character of all the groups (hydrazonic and pyridinic). In a recent qualitative analysis of the factor controlling the acidity of N–H bonds in amide compounds[15] $RC({=}X)NH_2$ (X = O, NH or S) three effects (field-inductive, polarizability and resonance) were used to explain this trend: (*a*) the field-inductive factor should decrease in the order of the dipole moments, which are C=S (2.95 D) > C=O (2.5 D); (*b*) the polarizability and (*c*) resonance effects should also be large for sulfur compounds because of the relative weakness of the C=S bond and the greater ability of sulfur with respect to oxygen to accommodate a negative charge. These three factors combine to make the NH hydrogens in H_2L^2 more acidic than the corresponding ones in H_2L^1; a similar but smaller decrease occurs in stepwise protonation constants for nitrogen in pyridine rings. If the methyl groups are replaced by phenyl, the resulting compounds are more acidic, as we can see by comparing the log K_n^{H} values of the present compounds, and those of bis(phenyl 2-pyridyl ketone) carbono- and thiocarbono-hydrazone [12.67(1), 8.08(2),

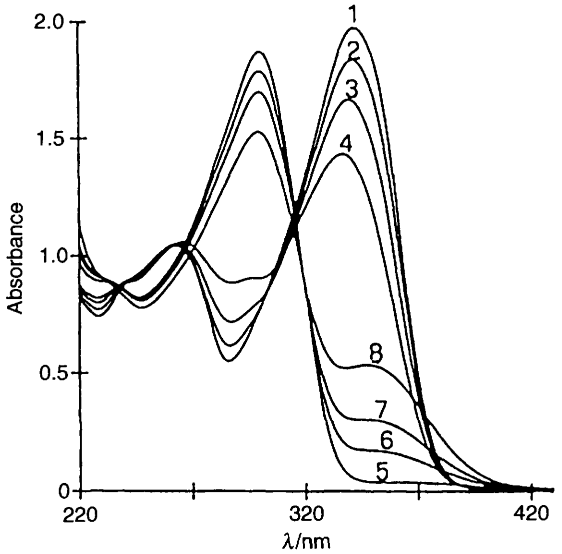

Fig. 1 Plots of experimental absorbance data *versus* wavelength for solutions [c_L 7.533 × 10^{-5}–7.271 × 10^{-5} mol dm^{-3}; pH 2.275 (1), 2.664 (2), 3.018 (3), 3.443 (4), 10.088 (5), 12.622 (6), 13.068 (7), 13.569 (8)] for H_2L^1 at 25 °C

3.74(3), 2.81(3); and 10.67(1), 5.42(3), 2.97(4)].[16] The sum of the squares of the residuals and the standard deviation in the absorbance data for the proligands (Table 1, 16 solutions, 211 wavelengths and 3376 points for H_2L^1; 17 solutions, 146 wavelengths and 2482 points for H_2L^2) were 5.962 × 10^{-2} and 5.0726 × 10^{-3} for H_2L^1 and 6.362 × 10^{-2} and 6.0329 × 10^{-3} for H_2L^2, *i.e.* the fit of the calculated spectra to the observed ones was very good. Typical absorption spectra for H_2L^1 (220–430 nm) are plotted in Fig. 1, in the range pH 2.275–13.569. When the pH increases from 2.275 to 3.443 small hypsochromic and high hypochromic shifts are observed [maximum, 1.979 *A* at 343 nm (1); 1.840 *A* at 342 nm (2); 1.670 *A* at 341 nm (3); 1.436 *A* at 338 nm (4)]. As the pH increases above 10.088 a simultaneous decrease in absorption and a maximum at 301 nm occurs (hypochromic effect) and a shoulder appears with increasing absorption (hyperchromic effect) and a maximum at 347–350 nm. There are two distinctive isosbestic points at 238 and 316 nm: the first corresponds to an equilibrium between the two species in which protonation of the pyridine nitrogens occurs, the second to the equilibrium between the species in which the hydrazonic nitrogens are involved. In Fig. 2 the molar absorption coefficients of the five species for each proligand obtained by use of the program SQUAD are plotted in the range 220–430 nm. By means of the positions of the absorption maxima it is possible to check the contribution of each species to the whole spectrum. In particular, it should be noted that the two systems exhibit slightly different trends, the maxima corresponding to H_2L^2 shifting to longer wavelengths (bathochromic effect) with increasing intensity (hyperchromic effect).

Both H_2L^1 and H_2L^2 have shown a noteworthy versatility giving rise to complexes with different stoichiometries in spite of similar experimental conditions. Probably they co-ordinate through the pyridinic, iminic and hydrazinic nitrogens as well as the sulfur or oxygen atom, yielding five-membered rings as in the structure of $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$, even if, under the same experimental conditions the metal to ligand ratio is different, related to the nature of the metal and the corresponding anion (chloride or acetate) used in the reaction. The ligands are able to form mono- and bi-nuclear complexes with copper chloride, while with zinc chloride only monometallic complexes have been obtained, probably because they are insoluble in the reaction medium and precipitate immediately: on the contrary, using $Zn(O_2CMe)_2$, it is possible to obtain also the bimetallic complex, namely $Zn_2(L^1)(O_2CMe)_2\cdot 4.5H_2O$, which is very soluble. The compound H_2L^2 is more acidic than H_2L^1 and this behaviour is maintained on complexation, so that it is monodeprotonated also in the monometallic complex $Cu(HL^2)Cl$.

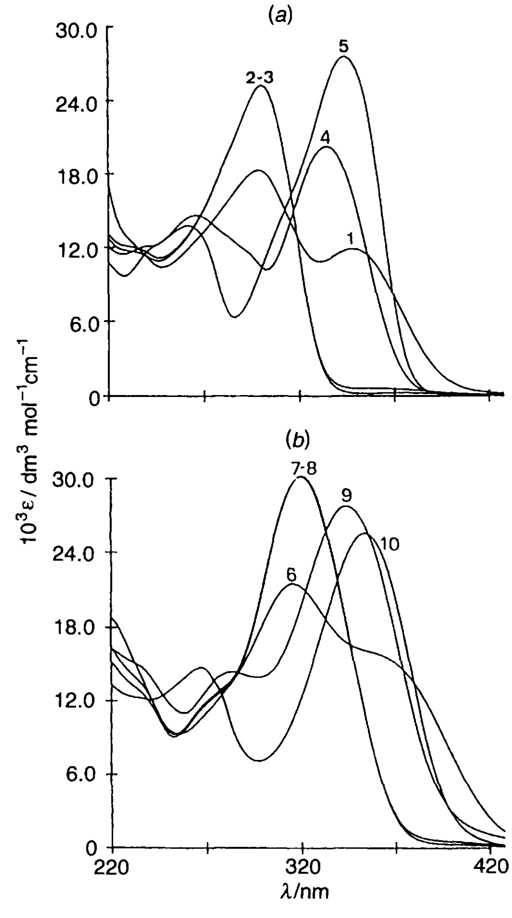

Fig. 2 Plots of the molar absorption coefficients (ε) of the five protonated species of (*a*) H_2L^1 and (*b*) H_2L^2: (1) ε_L, (2) ε_{HL}, (3) ε_{H_2L}, (4) ε_{H_3L}, (5) ε_{H_4L}, for H_2L^1; (6) ε_L, (7) ε_{HL}, (8) ε_{H_2L}, (9) ε_{H_3L}, (10) ε_{H_4L}, for H_2L^2

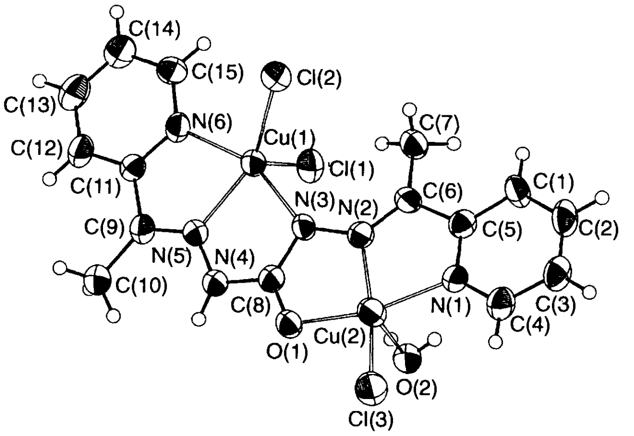

Fig. 3 An ORTEP[17] diagram and numbering scheme for $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres

As established by X-ray crystallographic analysis, the copper complex $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$ is dinuclear. A drawing of the molecule including the numbering scheme is shown in Fig. 3 and the main structural parameters are listed in Table 3, together with the corresponding values for the two proligands. The carbonohydrazone functions as a terdentate donor towards both metal centres [N,N,N for Cu(1) and O,N,N, for Cu(2)], which are both five-co-ordinate but with

Table 2 Summary of crystal data, intensity collection and refinement

	$[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$	H_2L^1	$H_2L^2\cdot 0.5MeOH$
Formula	$C_{15}H_{20}Cl_3Cu_2N_6O_{3.5}$	$C_{15}H_{16}N_6O$	$C_{15.5}H_{18}N_6O_{0.5}S$
M	573.81	296.33	328.41
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	11.606(4)	11.268(2)	38.945(9)
b/Å	11.396(4)	19.189(5)	7.259(2)
c/Å	8.847(3)	6.969(1)	23.574(6)
α/°	94.73(2)		
β/°	82.08(2)	96.13(1)	97.36(2)
γ/°	110.69(3)		
U/Å^3	1083.5(7)	1498.2(4)	6609(3)
Z	2	4	16
D_c/g cm^{-3}	1.76	1.31	1.32
Crystal dimensions (mm)	0.16 × 0.30 × 0.55	0.20 × 0.28 × 0.63	0.30 × 0.33 × 0.58
Diffractometer	Enraf-Nonius CAD-4	Siemens AED	Siemens AED
Radiation (λ/Å)	Mo-Kα (0.710 69)	Cu-Kα (1.541 84)	Cu-Kα (1.541 84)
μ/cm^{-1}	23.65	7.21	18.31
F(000)	578	624	2768
θ Range	3–30	3–70	3–70
Reflections measured	6321	3178	6272
Reflections unique	6321	2844	6269
Reflections observed [$F_o > 4\sigma(F_o)$]	3026	1482	1817
Parameters varied	282	264	410
$R1$ for observed data	0.0716	0.0392	0.0855
$wR2$ for all data*	0.2602	0.1296	0.2754

* Weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ with $P = [2F_c^2 + \max.(0,F_o^2)]/3$; a = 0.100 for $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$ and $H_2L^2\cdot 0.5MeOH$, 0.061 for H_2L^1.

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses in $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$, H_2L^1 and H_2L^2

(*a*) In co-ordination polyhedra of $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$

Cu(1)–Cl(1)	2.480(2)	Cu(2)–Cl(3)	2.221(2)	N(3)–Cu(1)–N(6)	156.5(2)	O(2)–Cu(2)–N(2)	87.6(2)
Cu(1)–Cl(2)	2.261(3)	Cu(2)–O(1)	1.948(6)	Cl(2)–Cu(1)–N(5)	143.0(2)	O(2)–Cu(2)–N(1)	89.4(2)
Cu(1)–N(3)	2.053(5)	Cu(2)–O(2)	2.525(7)	Cl(1)–Cu(1)–N(5)	106.4(2)	O(1)–Cu(2)–N(1)	161.9(2)
Cu(1)–N(5)	1.981(7)	Cu(2)–N(1)	1.951(7)	Cl(2)–Cu(1)–N(3)	102.6(2)	O(1)–Cu(2)–O(2)	86.2(2)
Cu(1)–N(6)	2.040(6)	Cu(2)–N(2)	1.962(5)	Cl(1)–Cu(1)–Cl(2)	109.9(1)	Cl(3)–Cu(2)–N(2)	165.6(2)
						Cl(3)–Cu(2)–O(2)	106.4(2)

(*b*) In the organic molecule

			H_2L^2	
$[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$		H_2L^1	A	B
O(1)–C(8)	1.249(8)	1.231(3)	1.667(6)*	1.652(5)*
N(2)–N(3)	1.390(8)	1.378(2)	1.380(7)	1.395(6)
N(2)–C(6)	1.275(10)	1.287(3)	1.273(7)	1.269(8)
N(3)–C(8)	1.357(10)	1.377(3)	1.354(6)	1.365(7)
N(4)–N(5)	1.363(7)	1.373(3)	1.373(6)	1.391(7)
N(4)–C(8)	1.348(10)	1.356(3)	1.358(7)	1.343(7)
N(5)–C(9)	1.282(10)	1.290(3)	1.298(8)	1.279(8)
C(5)–C(6)	1.495(10)	1.486(3)	1.489(9)	1.486(8)
C(9)–C(11)	1.480(9)	1.485(3)	1.492(9)	1.505(8)
N(2)–N(3)–C(8)	107.8(5)	118.4(2)	119.0(4)	119.3(4)
N(4)–N(5)–C(9)	123.5(6)	119.1(2)	117.4(5)	119.0(5)
N(3)–N(2)–C(6)	127.5(6)	117.3(2)	118.6(5)	117.1(5)
N(5)–N(4)–C(8)	116.0(6)	117.3(2)	118.6(5)	118.5(5)
N(3)–C(8)–N(4)	117.5(6)	114.5(2)	114.8(5)	114.3(5)

* S–C(8).

different environments, three N and two Cl for Cu(1) and two N, two O and one Cl for Cu(2). Differences also occur in the co-ordination polyhedra. As is mainly apparent from the bond angles in Table 3, the Cu(1) co-ordination sphere is rather irregular; it can be described as a distorted square pyramid with Cl(1) occupying the apical position (the four basal atoms are roughly coplanar within 0.33 Å) or, alternatively, as a distorted trigonal bipyramid with N(3) and N(6) in the axial positions [N(3)–Cu(1)–N(6) 156.5(2)°]. The co-ordination geometry at Cu(2) is approximately distorted square planar with the water oxygen O(2) at the apex.

It is interesting that while the free H_2L^1 is in the *E-Z* form (see Fig. 4), on complexation it rearranges so to the *E-E* one. Owing to the chelation effects, in the copper complex the ligand molecule as a whole has an approximately planar configuration, the dihedral angle between the two symmetrical parts being only 10.0(1)°. The structure is held together by hydrogen bonds which occur between N(4) and the co-ordinated water

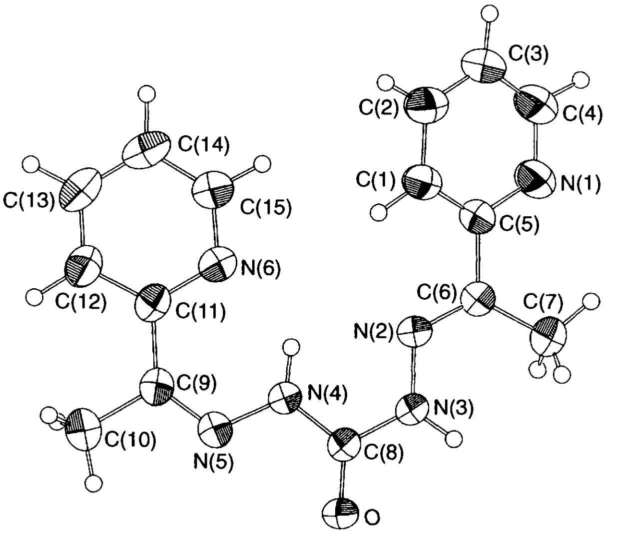

Fig. 4 An ORTEP diagram and numbering scheme for H_2L^1. Details as in Fig. 3

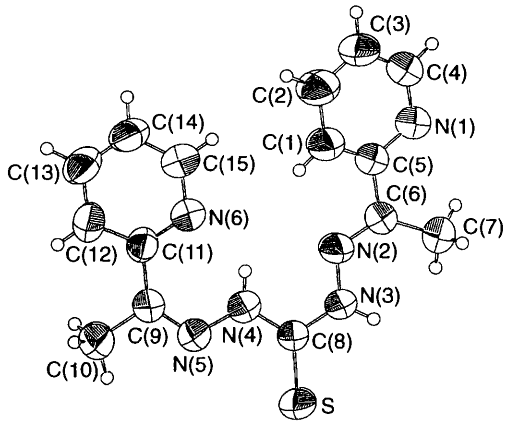

Fig. 5 An ORTEP diagram and numbering scheme for H_2L^2 (molecule A). Details as in Fig. 3

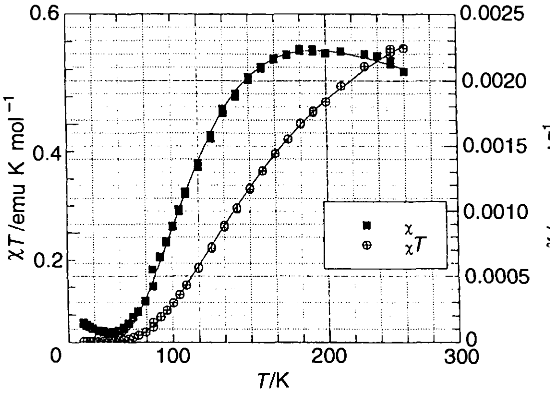

Fig. 6 Plots of χ_m and $\chi_m T$ *versus* T for $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$. The solid lines represent the best fit

molecule at $2 - x$, $1 - y$, $1 - z$ [N(4)···O(2) 2.770(9) Å, N(4)–H···O(2) 151°].

On the contrary, when H_2L^1 is free, it has a marked non-planar configuration, in which one of the two pyridine rings [N(1)···C(5)] is twisted with respect to the central system C(6)N(2)N(3)C(8)O(1)N(4)N(5)C(9) and forms an interplanar angle of 28.59(6)° with it, whereas the other pyridine ring [N(6)···C(15)] is nearly coplanar with the above system, the dihedral angle being 8.15(7)°. The H_2L^1 structure is characterized by the presence of an intramolecular N–H···N hydrogen bond [N(4)···N(6) 2.667(3) Å, N(4)–H···N(6) 131°] which is probably responsible for the stabilization of the *E-Z* isomer. In fact, the other two free carbazones, of known structure,[8] where this type of bond is not present, assume the 'more open' *E-E* form. The high ^1H NMR chemical shift of the hydrazinic hydrogen suggests that the intramolecular hydrogen bond is maintained in solution. Packing is mainly determined by N–H···O intermolecular hydrogen bonds [N(3)···O(1) at $-x$, $-y$, $1 - z$, 2.953(2) Å; N(3)–H···O(1) 163°].

The structure of H_2L^2 is strictly related to that of H_2L^1, but differs in having two symmetry-independent molecules in the asymmetric unit and half a molecule of MeOH cocrystallized with each molecule of H_2L^2. As the conformations of the two molecules are very similar, only molecule A is illustrated in Fig. 5. The crystalline cohesion is mainly ensured by intermolecular N···S interactions which could be considered as weak hydrogen bonds [molecule A: N(3)···S(1) $\frac{3}{2} - x$, $\frac{1}{2} - y$, $1 - z$, 3.542(5) Å, N(3)–H···S(1) 162°; molecule B: N(3)···S(1), $1 - x$, $1 - y$, $1 - z$, 3.622(5) Å, N(3)–H···S(1) 140°].

The room-temperature EPR spectrum of the complex $[Cu_2(HL^1)Cl_3(OH_2)]\cdot 1.5H_2O$ showed a single broad band (ΔH_{pp} = 200 G) with $g = 2.073$. The magnetic susceptibility χ is plotted in Fig. 6 as a function of temperature and shows a broad maximum at T = 190 K, a clear indication of a strong antiferromagnetic coupling between the two copper(II) ions. The best fit of the data ($R = 1.75 \times 10^{-3}$) was obtained with the parameters $g = 2.128$ and $J = 213.3$ cm^{-1} (the spin Hamiltonian which describes the coupling of two neighbouring spins is $\mathcal{H} = 2J\cdot S_1\cdot S_2$).

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References

1 C. J. Cairns and D. H. Busch, *Coord. Chem. Rev.*, 1986, **69**, 1.
2 R. D. Willet, D. Gatteschi and O. Kahn, *Magneto-Structural Correlations in Exchange Coupled Systems*, NATO ASI Series, 1985.
3 T. N. Sorrell, *Tetrahedron*, 1989, **45**, 3.
4 P. A. Vigato, S. Tamburini and D. E. Fenton, *Coord. Chem. Rev.*, 1990, **106**, 25.
5 A. Bacchi, L. P. Battaglia, M. Carcelli, C. Pelizzi, G. Pelizzi, C. Solinas and M. A. Zoroddu, *J. Chem. Soc., Dalton Trans.*, 1993, 775 and refs. therein.
6 D. X. West, S. B. Padhye and P. B. Sonawane, *Struct. Bonding (Berlin)*, 1991, **76**, 1.
7 S. R. Turk, C. Shipman, jun. and J. C. Drach, *Biochem. Pharmacol.*, 1986, **35**, 1539; *J. Gen. Virol.*, 1986, **67**, 1625.
8 T. A. Blumenkopf, J. A. Harrington, C. S. Koble, D. D. Bankston, R. W. Morrison, jun., E. C. Bigham, V. L. Styles and T. Spector, *J. Med. Chem.*, 1992, **35**, 2306.
9 C. Bustos, O. Burckhardt, R. Schrebler, D. Carrillo, A. M. Arif, A. H. Cowley and C. M. Nunn, *Inorg. Chem.*, 1990, **29**, 3996.
10 D. J. Leggett and W. A. E. McBryde, *Anal. Chem.*, 1975, **47**, 1065.
11 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, SIR 92, *J. Appl. Crystallogr.*, 1994, **27**, 435.
12 G. M. Sheldrick, SHELXL 92, Program for structure refinement, University of Göttingen, 1992.
13 A. Bacchi, F. Ferranti and G. Pelizzi, *Acta Crystallogr., Sect. C*, 1993, **49**, 1163.
14 M. T. Siles Cordero, A. Garcia de Torres and J. M. Cano Pavon, *Talanta*, 1993, **40**, 691.
15 F. G. Bordwell and G. Z. Ji, *J. Am. Chem. Soc.*, 1991, **113**, 8398.
16 E. Leporati, unpublished work.
17 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
18 J. Dan, S. Seth and S. Chakraborty, *Acta Crystallogr., Sect. C*, 1987, **43**, 1114; V. M. Kolb, P. D. Robinson and C. Y. Mayers, *Acta Crystallogr., Sect. C*, 1994, **50**, 417.

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