A New Polydentate Hydrazonic Ligand and its Dinuclear Copper(II) Complex with Different Co-ordination Environments *

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A new hydrazone derivative, di-2-pyridyl ketone [phenyl(semicarbazono)acetyl]hydrazone (H_2L), has been prepared and examined as a chelating agent towards metal ions. The molecular structure of the copper complex $[Cu_2LCl_2] \cdot H_2O$ consists of a pair of structurally distinct metal centres with different environments bound to the heptadentate hydrazonic ligand and held together by a $-N-N-$ bridge.

Di- and poly-nuclear metal complexes are of considerable interest because they provide the opportunity to study the intramolecular binding, magnetic exchange interactions, multi-electron redox reactions and possible activation of small substrate molecules.[1-6] Acylhydrazones, examined in our laboratory as ligands towards transition-metal elements, have shown ability to form di- or tetra-nuclear metal complexes containing $M-X-M$ ($X = Cl$, O or N) or $M-N-N-M$ systems.[7,8] In order to isolate di- or poly-metallic, homo- and hetero-nuclear complexes, we have projected and synthesised acylhydrazones by treating aldehydes or ketones with poly-dentate hydrazides of formula $RC(O)NHN=C(R')C(O)$-$NHNH_2$ ($R = NH_2$, 2-pyridyl or 2-hydroxyphenyl; $R' = CH_3$ or C_6H_5).[9,10]

The present paper describes the synthesis, thermal analysis, IR spectra and the X-ray diffraction analysis of H_2L, the first of a series of new ligands obtained from the reaction of di-2-pyridyl ketone with $H_2NC(O)NHN=C(C_6H_5)C(O)NHNH_2$, and its dinuclear copper complex $[Cu_2LCl_2] \cdot H_2O$, the magnetic properties and EPR spectra of which are also discussed.

Experimental

Materials.—Solvents were purified using published procedures.[11] Semicarbazide hydrochloride (Fluka), methyl benzoylformate (Aldrich), hydrazine hydrate (Fluka), and di-2-pyridyl ketone (Aldrich) were commercially available.

Preparations.—$H_2NC(O)NHN=C(C_6H_5)CO_2CH_3$. A solution of methyl benzoylformate (6.4 cm³) was added dropwise to a slight excess of semicarbazide hydrochloride (5.0 g, 44.8 mmol) in water–methanol (4:1 v/v, 100 cm³). The mixture was refluxed for about 1 h. A white crystalline product was isolated by slow evaporation of the solvents at room temperature. The crude product was filtered off, washed with chloroform and recrystallised from methanol, m.p. 182 °C, yield 80% (Found: C, 55.0; H, 4.2; N, 18.9. $C_{10}H_{11}N_3O_3$ requires C, 54.3; H, 5.0; N, 19.0%).

H_2L
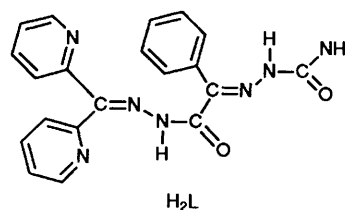
$H_2NC(O)NHN=C(C_6H_5)C(O)NHNH_2$. A suspension of the above product (5.7 g, 25.8 mmol) in an ethanol solution (5 cm³) of hydrazine hydrate (2 cm³) was stirred at room temperature for about 3 h. After cooling a white microcrystalline product was isolated, decomp. 193 °C, yield 42% (Found: C, 50.0; H, 5.1; N, 31.2. $C_9H_{11}N_5O_2$ requires C, 48.9; H, 5.0; N, 31.7%).

Di-2-pyridyl ketone [*(phenyl(semicarbazono)acetyl]hydrazone hydrate* $H_2L \cdot H_2O$. To a warm solution of $H_2NC(O)$-$NHN=C(C_6H_5)C(O)NHNH_2$ (1.80 g, 8.10 mmol) in ethanol–water (7:1 v/v, 150 cm³) was added an equimolar amount (1.5 g, 8.10 mmol) of di-2-pyridyl ketone. The solution was then refluxed for about 3 h. After cooling a crystalline solid was isolated, m.p. 196 °C, yield 75% (Found: C, 57.8; H, 4.6; N, 24.0. $C_{20}H_{19}N_7O_3$ requires C, 59.2; H, 4.7; N, 24.2%). Mass spectrum: m/z 237 (40), 168 (20), 146 (10), 105 (20), 91 (10) and 78 (100%). UV spectrum in 95% ethanol: 330 nm.

$[Cu_2LCl_2] \cdot H_2O$ **1**.—To an ethanol solution (50 cm³) of H_2L (0.5 g, 1.30 mmol) was added the appropriate amount of solid copper(II) chloride dihydrate (0.44 g, 1:2 molar ratio). After slow evaporation of the solvent at room temperature brown-greenish crystals were isolated, decomp. 215 °C, yield 70% (Found: C, 40.2; H, 3.0; N, 16.1. $C_{20}H_{17}Cl_2Cu_2N_7O_3$ requires C, 39.9; H, 2.8; N, 16.3%). Compound **1** was also isolated from the reaction of di-2-pyridyl ketone, $H_2NC(O)NHN=C(C_6H_5)$-$C(O)NHNH_2$ and copper(II) chloride dihydrate (1:1:2 molar ratio) in ethanol solution (yield 58%).

Measurements.—Elemental C, H and N analyses were carried out on Perkin Elmer model 240 automatic equipment. Infrared spectra (4000–400 cm⁻¹) for KBr discs were recorded on a Nicolet 5 PC FT-IR spectrometer, mass spectra on a Varian CH-5 spectrometer [70 eV (*ca.* 1.12–10⁻¹⁷ J)], and electronic

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Table 1 Fractional coordinates (× 10⁴) for non-hydrogen atoms, with estimated standard deviations (e.s.d.s) in parentheses for compound 1

Atom	X/a	Y/b	Z/c
Cu(1)	3360.5(8)	5379.4(5)	5230.4(5)
Cu(2)	−180.3(8)	3440.1(4)	5230.3(5)
Cl(1)	1515(1)	2348(1)	5008(1)
Cl(2)	−2218(1)	2982(1)	4704(1)
O(1)	434(4)	4014(2)	4025(2)
O(2)	5048(4)	5995(2)	4949(2)
N(1)	3252(5)	5319(3)	6603(3)
N(2)	−508(4)	3338(3)	6609(3)
N(3)	1139(4)	4245(2)	5714(3)
N(4)	1801(4)	4703(3)	5086(3)
N(5)	3209(4)	5392(3)	3882(3)
N(6)	4094(5)	5881(3)	3446(3)
N(7)	5867(6)	6770(4)	3780(5)
C(1)	2181(6)	4964(3)	7051(3)
C(2)	1831(7)	5224(4)	7939(4)
C(3)	2661(8)	5812(4)	8382(4)
C(4)	3804(9)	6112(4)	7944(4)
C(5)	4042(7)	5865(4)	7044(4)
C(6)	1330(5)	4329(3)	6599(3)
C(7)	511(5)	3716(3)	7122(4)
C(8)	737(7)	3476(4)	8030(4)
C(9)	−150(7)	2929(4)	8442(4)
C(10)	−1243(7)	2627(4)	7951(4)
C(11)	−1351(6)	2827(3)	7018(4)
C(12)	1428(6)	4494(3)	4188(3)
C(13)	2277(6)	4914(3)	3478(3)
C(14)	2105(6)	4758(3)	2480(4)
C(15)	2565(10)	5317(5)	1841(5)
C(16)	2447(15)	5154(6)	902(5)
C(17)	1878(13)	4445(6)	590(5)
C(18)	1370(9)	3899(5)	1211(5)
C(19)	1484(7)	4052(4)	2154(4)
C(20)	4998(6)	6214(3)	4099(4)
O(3)	608(10)	7976(6)	6830(7)

Table 2 Fractional coordinates (× 10⁴) for non-hydrogen atoms with e.s.d.s in parentheses for $H_2L \cdot H_2O$

Atom	X/a	Y/b	Z/c
O(1)	4 021(1)	7 981(2)	2 589(2)
O(2)	−10(2)	2 207(2)	−1 410(2)
O(3)	4 485(2)	11 093(3)	4 389(3)
N(1)	101(2)	6 685(2)	4 748(2)
N(2)	1 392(1)	9 433(2)	8 609(2)
N(3)	2 511(1)	8 381(2)	4 930(2)
N(4)	2 203(1)	7 464(2)	3 469(2)
N(5)	1 766(1)	5 207(2)	978(2)
N(6)	1 322(2)	4 142(2)	−310(2)
N(7)	91(2)	3 210(2)	1 211(2)
C(1)	372(2)	8 061(2)	5 551(2)
C(2)	−478(2)	8 944(2)	6 033(2)
C(3)	−1 671(2)	8 396(3)	5 669(3)
C(4)	−1 965(2)	6 984(3)	4 887(3)
C(5)	−1 069(2)	6 180(3)	4 449(3)
C(6)	1 670(2)	8 638(2)	5 890(2)
C(7)	2 058(2)	9 617(2)	7 471(2)
C(8)	3 084(2)	10 617(2)	7 745(2)
C(9)	3 433(2)	11 424(2)	9 255(2)
C(10)	2 747(2)	11 256(2)	10 430(2)
C(11)	1 729(2)	10 262(2)	10 055(2)
C(12)	3 030(2)	7 285(2)	2 391(2)
C(13)	2 643(2)	6 123(2)	901(2)
C(14)	3 317(2)	6 110(2)	−489(2)
C(15)	3 904(2)	4 987(2)	−1 270(2)
C(16)	4 595(2)	5 038(3)	−2 506(3)
C(17)	4 686(2)	6 169(3)	−2 970(3)
C(18)	4 098(2)	7 285(3)	−2 213(3)
C(19)	3 431(2)	7 253(2)	−970(3)
C(20)	416(2)	3 108(2)	−210(2)

Table 3 Selected bond distances (Å) for complex 1 and ligand H_2L

(a) In the co-ordination polyhedra of 1

Cu(1)–O(2)	1.959(4)	Cu(2)–O(1)	2.068(4)
Cu(1)–N(1)	1.988(4)	Cu(2)–N(2)	2.025(4)
Cu(1)–N(4)	1.877(4)	Cu(2)–N(3)	1.954(4)
Cu(1)–N(5)	1.951(4)	Cu(2)–Cl(1)	2.443(2)
		Cu(2)–Cl(2)	2.230(2)

(b) In the ligand molecule

	1	H_2L
O(1)–C(12)	1.260(6)	1.218(2)
O(2)–C(20)	1.280(7)	1.225(2)
N(3)–N(4)	1.342(6)	1.372(2)
N(3)–C(6)	1.297(6)	1.288(2)
N(4)–C(12)	1.384(6)	1.344(3)
N(5)–N(6)	1.331(6)	1.355(2)
N(5)–C(13)	1.322(7)	1.286(2)
N(6)–C(20)	1.389(7)	1.395(3)
N(7)–C(20)	1.323(8)	1.332(3)
C(1)–C(6)	1.472(7)	1.492(2)
C(6)–C(7)	1.486(7)	1.491(2)
C(12)–C(13)	1.486(7)	1.504(2)
C(13)–C(14)	1.472(7)	1.484(3)

spectra (900–300 nm) on a Kontron UVIKON 860 spectrophotometer. The thermogravimetric analysis was made with a Perkin Elmer Delta series TGA 7 thermobalance from 30 to 400 °C at a rate of 20 °C min⁻¹. Magnetic susceptibility was measured at room temperature using a Bruker B-MB4 Faraday system with a Cahan 1000 electrobalance using $Hg[Co(SCN)_4]$ as a calibrant and correcting for diamagnetism with the appropriate Pascal constants. The EPR spectra at 298 and 77 K were obtained using a Bruker ER 220D-SRC spectrometer. The microwave frequency was calibrated against powder diphenylpicrylhydrazyl (dpph, g = 2.0036).

X-Ray Crystallography.—X-Ray measurements were carried out for both compounds at room temperature on a computer-controlled Siemens AED diffractometer using nickel-filtered Cu-Kα radiation for 1 and niobium-filtered Mo-Kα radiation for $H_2L \cdot H_2O$.

Crystal data for complex 1. 0.20 × 0.24 × 0.39 mm, $C_{20}H_{17}$-$Cl_2Cu_2N_7O_3$, M = 601.40, monoclinic, space group $P2_1/n$, a = 9.644(1), b = 16.345(5), c = 14.438(3) Å, β = 90.52(1)°, U = 2275.8(9) Å³, Z = 4, D_c = 1.755 g cm⁻³, $F(000)$ = 1208, μ(Cu-Kα) = 48.3 cm⁻¹. 4220 Reflections measured to $2\theta_{max}$ 130°, 3176 observed with $I > 2\sigma(I)$.

Crystal data for $H_2L \cdot H_2O$. 0.65 × 0.76 × 0.80 mm, $C_{20}H_{19}$-N_7O_3, M = 405.42, triclinic, space group $P\bar{1}$, a = 11.260(2), b = 10.261(2), c = 9.208(2) Å, α = 109.53(2), β = 89.91(2), γ = 97.85(2)°, U = 992.2(4) Å³, Z = 2, D_c = 1.357 g cm⁻³, $F(000)$ = 424, μ(Mo-Kα) = 0.9 cm⁻¹. 4356 Reflections measured to $2\theta_{max}$ 54°, 3174 observed with $I > 2\sigma(I)$.

In each case no crystal decay was observed. The intensities were processed with the peak-profile procedure following a local modification of the Lehmann and Larsen method[12] and the data were corrected for Lorentz and polarisation effects. For

complex 1 the empirical method of Walker and Stuart[13] was also applied during the refinement to account for absorption effects.

Both structures were solved by a combination of direct methods and Fourier difference techniques and refined by full-matrix least-squares procedures, with all non-hydrogen atoms treated anisotropically to give final R of 0.050 and 0.048 for 1 and $H_2L \cdot H_2O$ respectively. The hydrogen atoms, the positional parameters of which were obtained from Fourier difference maps, except those belonging to the water molecules which were ignored, and three atoms of H_2L which were placed at calculated 'riding' positions, were refined isotropically. The

Table 4 Selected bond angles (°) in complex 1 and ligand H_2L

(a) In the co-ordination polyhedra of 1

N(4)–Cu(1)–N(5)	80.9(2)	Cl(1)–Cu(2)–O(1)	91.4(1)
N(1)–Cu(1)–N(5)	172.3(2)	Cl(1)–Cu(2)–Cl(2)	107.4(1)
N(1)–Cu(1)–N(4)	91.9(2)	Cu(2)–O(1)–C(12)	110.4(3)
O(2)–Cu(1)–N(5)	81.0(2)	Cu(1)–O(2)–C(20)	108.5(3)
O(2)–Cu(1)–N(4)	161.1(2)	Cu(1)–N(1)–C(5)	114.1(4)
O(2)–Cu(1)–N(1)	106.5(2)	Cu(1)–N(1)–C(1)	123.0(4)
N(2)–Cu(2)–N(3)	79.1(2)	Cu(2)–N(2)–C(11)	126.9(4)
O(1)–Cu(2)–N(3)	78.8(2)	Cu(2)–N(2)–C(7)	112.1(3)
O(1)–Cu(2)–N(2)	155.9(2)	Cu(2)–N(3)–C(6)	120.6(3)
Cl(2)–Cu(2)–N(3)	156.4(1)	Cu(2)–N(3)–N(4)	116.5(3)
Cl(2)–Cu(2)–N(2)	99.3(1)	Cu(1)–N(4)–N(3)	129.7(3)
Cl(2)–Cu(2)–O(1)	97.1(1)	Cu(1)–N(4)–C(12)	116.8(3)
Cl(1)–Cu(2)–N(3)	96.0(1)	Cu(1)–N(5)–C(13)	118.6(3)
Cl(1)–Cu(2)–N(2)	100.3(1)	Cu(1)–N(5)–N(6)	115.8(3)

(b) In the ligand molecule

|	1	H_2L
N(4)–N(3)–C(6)	122.9(4)	117.7(2)
N(3)–N(4)–C(12)	112.0(4)	119.2(2)
N(6)–N(5)–C(13)	125.6(4)	120.3(2)
N(5)–N(6)–C(20)	108.4(4)	120.2(2)
N(1)–C(1)–C(6)	121.0(4)	117.0(2)
C(2)–C(1)–C(6)	118.9(5)	119.4(2)
N(3)–C(6)–C(1)	125.8(5)	126.0(2)
C(1)–C(6)–C(7)	123.2(4)	118.5(2)
N(3)–C(6)–C(7)	110.9(4)	115.5(2)
N(2)–C(7)–C(6)	114.3(4)	115.6(2)
C(6)–C(7)–C(8)	126.3(5)	121.9(2)
O(1)–C(12)–N(4)	121.3(4)	123.8(2)
N(4)–C(12)–C(13)	113.1(4)	114.4(2)
O(1)–C(12)–C(13)	125.6(4)	121.8(2)
N(5)–C(13)–C(12)	110.2(4)	115.6(2)
C(12)–C(13)–C(14)	122.6(5)	118.0(2)
N(5)–C(13)–C(14)	127.2(5)	126.4(2)
C(13)–C(14)–C(19)	121.5(5)	120.2(2)
C(13)–C(14)–C(15)	120.5(5)	120.8(2)
N(6)–C(20)–N(7)	115.4(5)	115.6(2)
O(2)–C(20)–N(7)	120.5(5)	126.2(2)
O(2)–C(20)–N(6)	124.1(5)	118.2(2)

quantity minimised was $\Sigma w(F_o - F_c)^2$, where the weighting scheme $w = k/[\sigma^2(F_o) + gF_o^2]$ was applied [$k = 2.9187(1)$, 1 ($H_2L·H_2O$); $g = 0.00531(1)$, 0.017 692 ($H_2L·H_2O$)]. Atomic scattering factors for neutral atoms were employed and the real and imaginary parts of the anomalous scattering effects were included for all non-hydrogen atoms.

Calculations were performed on a GOULD 6040 computer using the program packages SHELX 76,[14] SHELX 86,[15] PARST,[16] and ORTEP.[17] Final positional parameters for non-hydrogen atoms of complex 1 and H_2L are in Tables 1 and 2, respectively, selected bond distances and angles for both compounds in Table 3 and 4.

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

Results and Discussion

The X-ray structural analysis carried out on $[Cu_2LCl_2]·H_2O$ 1, which is the first metal complex of this series of new acylhydrazones, revealed the ability of the ligand in the chelation of two copper ions and in the production of dinuclear entities. It is noteworthy that the complex is obtained in high yield from a direct reaction between H_2L and $CuCl_2·2H_2O$ as well as from a template reaction between di-2-pyridyl ketone, $H_2NC(O)NHN=C(C_6H_5)C(O)NHNH_2$ and $CuCl_2·2H_2O$. Another indication of the high stability of the complex derives from the reactions carried out between H_2L and $CuCl_2·2H_2O$ in the presence of the chloride of a second metal species (e.g. Ni or

dpph
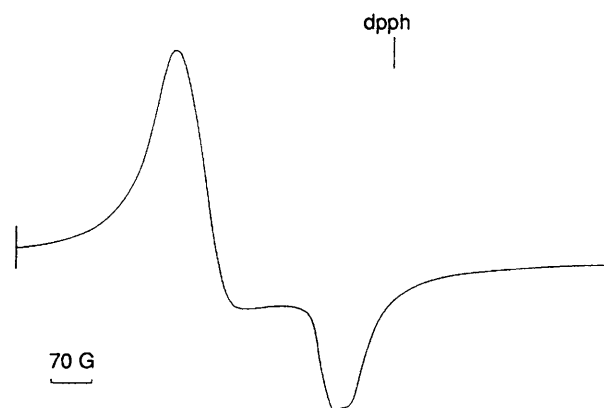
Fig. 1 X-Band EPR spectrum of a polycrystalline sample of compound 1 at room temperature

70 G
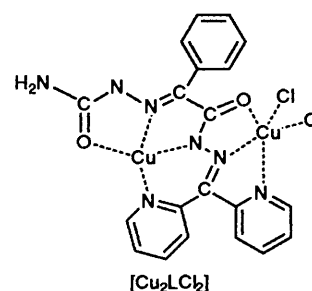
[Cu₂LCl₂]

Co, 1:1:1 molar ratio). In all cases $[Cu_2LCl_2]·H_2O$ was isolated as unique or prevalent reaction product. Thermogravimetric analysis (TGA) in the range 30–400 °C revealed the complex is stable until its decomposition temperature at 215 °C. A comparison between the thermograms of H_2L and $[Cu_2LCl_2]·H_2O$ shows the increased thermal stability ($\Delta T \approx 20$ °C) induced by the co-ordination effect and the polymeric nature of the complex.

The main vibrational bands of the two compounds are as follows: 1, $v(NH_2)$ 3493, $v(NH)$ 3302, 3124, amide I 1649, amide II 1598; H_2L, $v(NH_2)$ 3557, $v(NH)$ 3343, 3133, amide I 1715, 1664, amide II 1591, 1510 cm⁻¹. As regards the $-C(O)N-N-$ moiety significant shifts are observed in agreement with the bideprotonated nature of the ligand as well as with the participation of both the CO groups in the co-ordination.[18-21] In particular, the frequency values of the CO groups, which can be better distinguished in the spectrum of the unco-ordinated ligand, undergo a negative shift as a consequence of the above-mentioned effects. Only one absorption at ca. 485 nm is observed in the electronic spectrum of $[Cu_2LCl_2]·H_2O$ in ethanol solution, despite the presence of two copper centres with different environments.

The polycrystalline powder EPR spectrum of the complex (Fig. 1) is not easily referred to standard triplet spectra, in the sense that it is not easy to assign parallel and perpendicular components or $\Delta m = \pm 1$, ± 2 transitions. This behaviour is very similar to that reported for some di-μ-hydroxo-bridged copper(II) compounds.[22] In our spectrum for the signal at about 3200 G we can calculate three g values, 2.20, 2.095 and 2.038. The most important signal is that at about 1300 G (Fig. 2) which shows that there is a weak exchange coupling between the two copper(II) ions Cu(1) and Cu(2), even when the susceptibility measurement gave a 'normal' magnetic moment around 1.7 at room temperature.

The structure of complex 1 consists of neutral complex molecules $[Cu_2LCl_2]$ and solvating H_2O molecules. The most important aspect is the presence of two structurally distinct types of copper(II) ions which are held together by a $-N-N-$ bridge. Fig. 3 shows an ORTEP view of the complex molecule with the atom labelling scheme used. Atom Cu(1) is four-co-
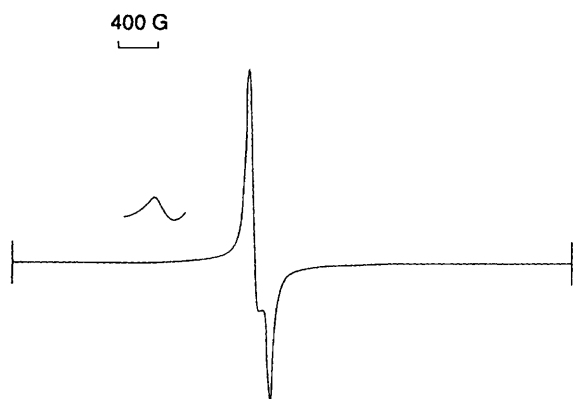
400 G
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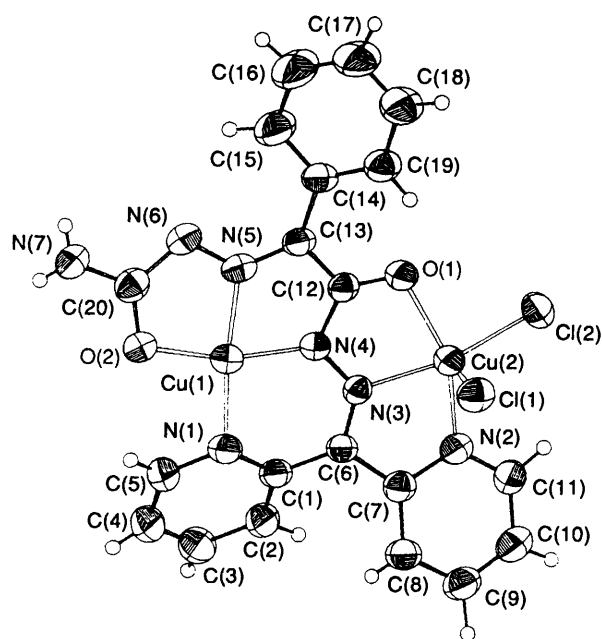Fig. 2 X-Band EPR spectrum of a polycrystalline sample of compound 1 at 77 K

Fig. 3 An ORTEP diagram and numbering scheme for compound 1. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres
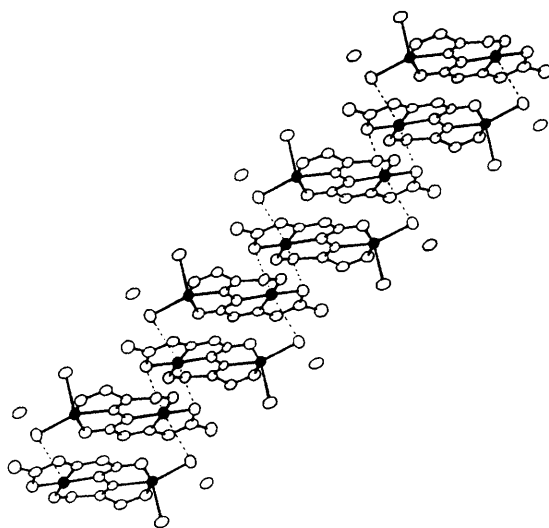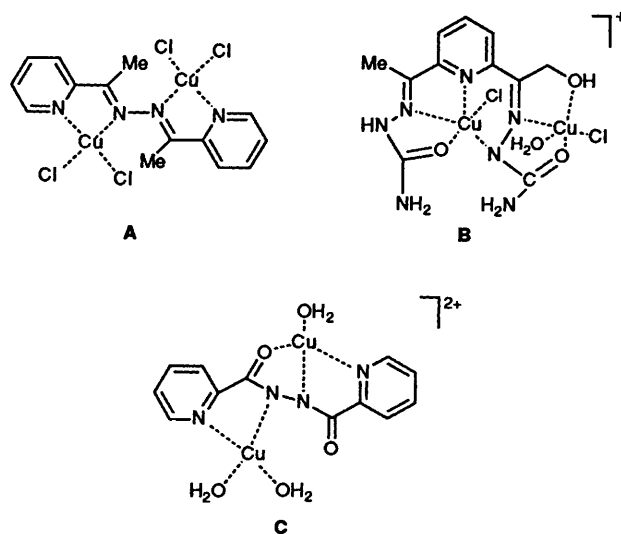

Fig. 4 Perspective view of compound 1 showing its polymeric nature. The aromatic rings have been omitted for clarity

A

B

C

ordinate and its environment is square planar involving three N and one O atom of the hydrazone molecule. The copper atom and these four donors are approximately coplanar, the maximum deviation being 0.07 Å. Two additional interactions from two neighbouring molecules give rise to two weak bonds Cu···O(2) (1 − x, 1 − y, 1 − z) and Cu···Cl(2) (−x, 1 − y, 1 − z), of length 2.734(4) and 2.899(2) Å, respectively, which link the molecules into polymeric units (Fig. 4) and give Cu(1) a tetragonally distorted octahedral environment. Such behaviour is consistent with the plasticity properties of the copper(II) co-ordination sphere,[23] as well as with the Jahn–Teller or pseudo-Jahn–Teller effect. The stereochemistry at Cu(2) is essentially five-co-ordinate square-based pyramidal with two N and one O atom from the hydrazone molecule and a Cl atom at the corners of a slightly tetrahedrally distorted square, while the other Cl atom occupies the apex of the pyramid. Atom Cu(2) is displaced by 0.35 Å from the mean basal plane towards the apical ligand. The two Cu–Cl distances differ by a significant 0.21 Å, a value which agrees satisfactorily with the difference usually found for axial and equatorial copper–chlorine bonds {e.g. 0.18 Å in cis-[bis(dimethyl-aminoethyl) ether]dichlorocopper[24] and 0.27 Å in [μ-2,7-bis(2-pyridyl)-1,8-naphthyridine](μ-chloro)dichloro(μ-hydroxo)di-copper,[25] both of which have a N₂OCl basal plane}.

A search carried out by means of the Cambridge Crystallographic Database indicated that, with the exception of three compounds, in all the structures consisting of a binuclear arrangement of two copper(II) atoms linked by a –N–N– bridge the N–N linkage is part of an heterocyclic system, i.e. phthalazine, pyridazine, pyrazole or triazole. The three compounds which afford the best comparison with the present one are A,[26] B[27] and C[28]. Particularly significant in these compounds is the torsion angle about the N–N linkage (70.8 in A, 173.7 in B, 169.3 in C, and 166.6° in compound 1) as it gives an indication of the planarity of the system and is also an important factor in determining the extent of coupling of the two metal centres. The Cu···Cu distances in our compound are: Cu(1)···Cu(2) 4.659(1), Cu(1)···Cu(1) (1 − x, 1 − y, 1 − z) 3.467(2), and Cu(1)···Cu(2) (−x, 1 − y, 1 − z) 3.679(1) Å.

The hydrazone molecule functions as a bideprotonated ligand and is arranged so as to accommodate two metal centres through the chelating action of seven donor atoms, by virtue of which four five-membered and one six-membered chelate rings are formed. Of particular interest is the conformation the hydrazone assumes in the co-ordinated form as compared to that found for the free ligand (Fig. 5): in the former a rotation around the C(6)–C(7) and C(20)–N(6) bonds occurs which allows N(2) and O(2) to be involved in the co-ordination and, at the same time, evidences the flexible nature of the molecule. In
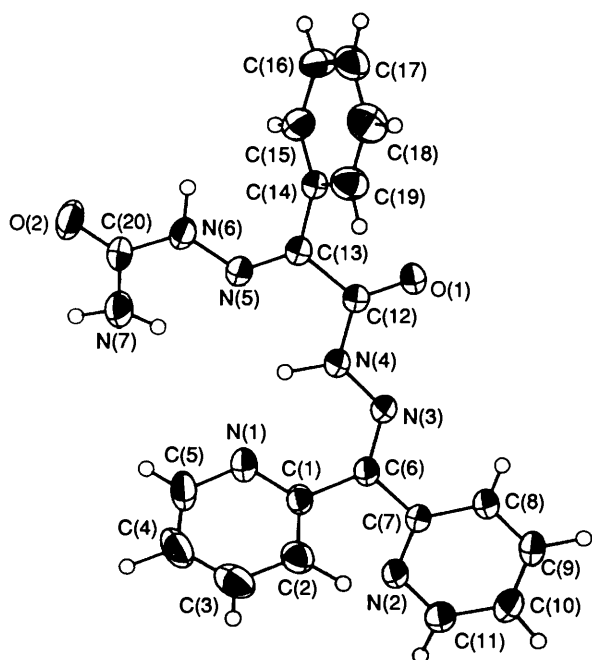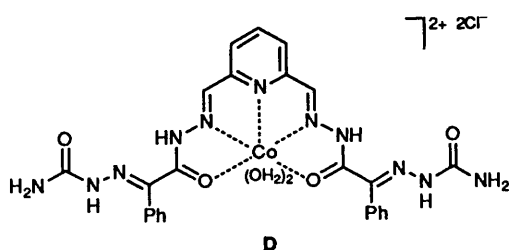
Fig. 5 An ORTEP diagram and numbering scheme for ligand H₂L. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by arbitrarily small spheres

D

both forms the hydrazone has a non-planar configuration and can be described in terms of four near-planar parts containing the three aromatic moieties, all of which are planar within experimental error, and the N(7)C(20)O(2)N(6)N(5)C(13)-C(12)N(4)O(1)N(3) system for which the maximum displacement is 0.18 Å in the co-ordinated form and 0.40 Å in the unco-ordinated one. The mean plane running through these ten atoms makes angles of 26.3(2), 10.2(2) and 25.7(2)° with the N(1)···C(5), N(2)···C(11), and C(14)···C(19) ring planes, respectively, in the copper complex. The corresponding values for the free ligand are 53.75(6), 13.58(7) and 57.16(7)°. The two pyridine ring planes are mutually inclined by 36.4(2) in the former and 64.19(8)° in the latter.

This is the first H₂L metal complex for which the crystal structure has been determined, so no comparisons are possible. However, as far as the above ten-atom system is concerned, mention can be made of two bis(hydrazone) complexes previously characterised by X-ray diffraction, namely [CoL'-(OH₂)₂]Cl₂·4.5H₂O D¹⁰ and [{Ni(H₂L″)(OH₂)Cl}₂Cl₂]·2dmf·5H₂O{H₄L″ = 2,6-diacetylpyridine bis[2-(semicarbazono)propionylhydrazone], dmf = dimethylformamide}.⁹ In the former no atom of the semicarbazone system, which is exactly the same as here, is involved in the co-ordination to cobalt, whereas in the latter, where a methyl group replaces the phenyl ring at C(13), four atoms of the system are bonded to nickel.

The crystalline cohesion in the copper compound is ensured by parallel base stackings as well as a hydrogen-bonding network involving as donors the amino group and the water molecule and as acceptors both the chlorine atoms and the water molecule itself: N(7)···Cl(1) (1 − x, 1 − y, 1 − z)

3.382(7), N(7)···O(3) (½ + x, ³⁄₂ − y, z − ½) 2.854(12), and O(3)···Cl(2) (−x, 1 − y, 1 − z) 3.135(10); N(7)–H(15)···Cl(1) 163(5) and N(7)–H(14)···O(3) 161(6)°.

The structure of the free ligand is characterised by the presence of an intramolecular NH···N hydrogen bond between N(4) and N(1) [N(4)···N(1) 2.781(3) Å, N(4)–H···N(1) 119(2)°]. The molecular packing is mainly dictated by a three-dimensional network of N–H···N and O–H···O hydrogen bonds where the donors are the amino group and the water molecule and the acceptors are the pyridine nitrogen N(2) and the carbonyl oxygen O(1). The water molecule acts as a symmetrical bridge between two ligand molecules: N(7)···N(2) (−x, 1 − y, 1 − z) 3.093(3), O(3)···O(1) 3.038(3) and O(3)···O(1) (1 − x, 2 − y, 1 − z) 3.048(3) Å; N(7)–H···N(2) 174(2)°.

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