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FULL PAPER

Ligand behaviour and reactivity of phenyl 2-pyridyl ketone azine. Structures of two polymorphic forms of the azine and a copper complex of the 3-phenyltriazolo[1,5-*a*]pyridine *

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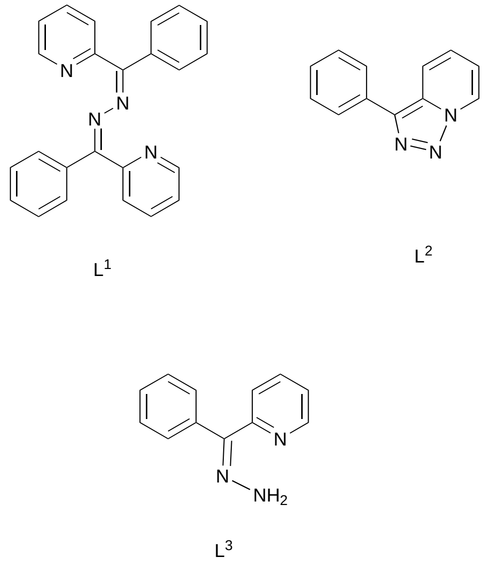
Two polymorphic forms of phenyl 2-pyridyl ketone azine (L^1) and the complex [ZnL^1Cl_2] have been synthesized and characterized by X-ray diffraction analysis. In the reaction with copper(II) chloride both isomers of the azine undergo hydrolytic and oxidative processes, giving rise to the complex [$CuL^2{}_2Cl_2$] (L^2 = 3-phenyltriazolo[1,5-*a*]pyridine). In order to clarify this process, phenyl 2-pyridyl hydrazone (L^3) has been synthesized and treated with copper(II) chloride; in this way $CuL^2(Cl)\cdot H_2O$ and CuL^3Cl_2 were isolated.

Azines represent a well known class of organic compounds, derived from the condensation of an aldehyde or ketone with hydrazine. The conditions for the synthesis which are generally simple and the possibility to obtain symmetrical or asymmetrical azines by using two identical or different carbonyl compounds make them appealing for many applications in different fields: salicylaldazine was studied as a molecular electronic device owing to its strongly luminescent and thermochromic properties in the solid state,[1] syringaldazine {[$HOC_6H_2(OMe)_2$-$CH{=}N]_2$} was proposed for the colorimetric determination of chlorine in water[2] and 4-bromo-4′-methoxyacetophenone azine showed strong second harmonic generation;[3] some examples of macrocyclic bis(azines)[4] and ferroelectric liquid crystals containing *ortho*-palladated azines[5] were also reported. Moreover the co-ordination chemistry of azines has produced a lot of different monometallic[6,7] and homo-[7,8] or hetero-bimetallic complexes with interesting magnetic properties.[9]

Pursuing our studies on the reactivity of hydrazones[10] and azines,[11] here we report on the characterization of the conformational polymorphism[12] and reactivity of phenyl 2-pyridyl ketone azine (L^1, Scheme 1). The ligand behaviour of L^1 was investigated towards zinc and copper ions. Since the reaction with copper(II) chloride led to a complex containing 3-phenyltriazolo[1,5-*a*]pyridine (L^2, Scheme 1) as ligand and taking into account our previous results on the formation of triazolo[1,5-*a*]pyridine by oxidation of the corresponding hydrazone,[10] we have also examined the reactivity of phenyl 2-pyridyl hydrazone (L^3, Scheme 1) towards copper(II) chloride.



Scheme 1

Results and Discussion

When phenyl 2-pyridyl ketone was treated with hydrazine in 2:1 molar ratio two products were obtained (L^1, **A** and **B**), characterized by identical elemental analyses and mass spectra and very similar IR spectra: a crystal structure determination revealed that they are two different conformers of the same geometrical *Z*,*Z* isomer. It is possible to have different geometrical isomers around the two C=N double bonds (*Z*,*Z*; *Z*,*E*; *E*,*E*), and different conformers, because the torsional barrier around the N–N bond is low. In general, in the azines the configuration is governed by steric factors,[13] so normally the phenyl ring and the other C=N group are, as in our case, *trans*. Relevant exceptions are the dichloropropiophenone azine,[14] in which the sterically demanding Cl_2CH_2 groups force the rings into a *cis* configuration, and the *o*-nitroacetophenone azine,[15] for which it was possible to determine the structures of both the *E*,*E* and *E*,*Z* isomers. If we focus on the stereochemistry around the N–N bond, in the literature a lot of azines are described with s-*trans* or *gauche* conformation, but, as far as we know, only in the two cases of methyl *p*-tolyl ketone azine[13] and 3-acetyl-4-(2-chlorophenyl)-4-hydroxy-2-methoxycrotonic acid lactone azine,[16] both the N–N s-*trans* and *gauche* conformers have been characterized by X-ray diffraction. This is also the case of **A** and **B**: the two polymorphic forms of L^1 are depicted in Figs. 1 and 2, where the unlabelled atoms are related to the other ones in **A** by a two-fold axis perpendicular to the bond N(2)–N(2A) and passing through its middle point, and in **B** by an inversion centre at the same point. The main crystallographic differences between the two compounds are: (1) the C(7)–N(2)–N(2A)–C(7A) torsional angle is 123.4(2) for **A** (*gauche*) and 180° for **B** (s-*trans*); (2) the orientation of the pyridyl ring points toward the imine bond in **A** [N(2)–C(7)–C(8)–N(1) 63.8(2)°] and 'outside' in **B** [N(2)–C(7)–C(8)–N(1) −114.7(2)°]; (3) the N–N bond distance is shorter for the *gauche* than for the *trans* form [1.386(2) in **A** and 1.416(2) Å in **B**], as already noted.[18]

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* Dedicated to the memory of Professor Luigi Pietro Battaglia.

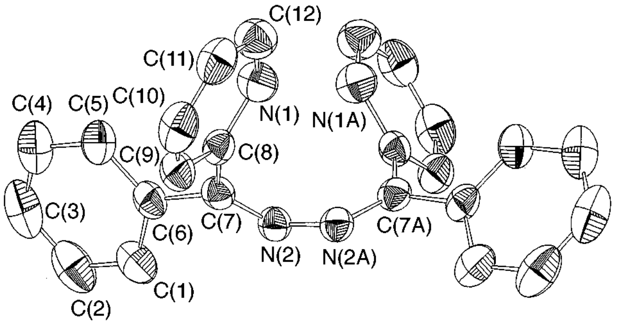

Fig. 1 An ORTEP[17] diagram for product **A**; thermal ellipsoids are drawn at the 40% probability level and hydrogens atoms are omitted

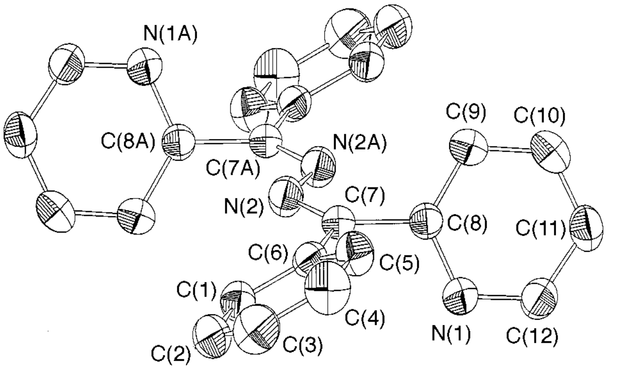

Fig. 2 An ORTEP diagram for product **B**; details as in Fig. 1

Computational studies were carried out on L^1 by using several force fields to estimate the energy of the different conformers. Systematic search (TRIPHOS 5.x), genetic algorithm and the Monte Carlo method were used. The systematic search showed that the s-*trans* conformer **B** is more stable than **A** by less than 2 kcal mol^{-1} (*ca.* 8.368 kJ mol^{-1}), so that small differences in packing interactions could make possible the cocrystallization.[13]

It is of note that, contrarily to the already quoted examples, from ^{13}C NMR data it is possible to conclude that in solution **A** and **B** are in equilibrium: if a sample of pure **A** or **B** is dissolved in $CDCl_3$ the two isomers are present in the final solution.

2-Pyridyl azines, reacting with a metal atom, assume *E*,*Z* configuration in mononuclear complexes,[6,7] and *E*,*E* in binuclear complexes.[7,8] When L^1 reacted with $ZnCl_2$ well formed orange crystals were obtained, characterized as $[ZnL^1Cl_2]$. A single-crystal X-ray diffraction analysis confirmed that in the complex the ligand undergoes *E*/*Z* isomerization with rotation about the N–N bond and inversion at N so as to act as a tridentate chelating agent; the zinc atom is therefore surrounded by three nitrogen atoms from the ligand and two chlorine atoms in a distorted trigonal bipyrimdal co-ordination geometry (Fig. 3). In particular, the equatorial positions are occupied by Cl(2), N(1) and N(4), the apical ones by Cl(1) and N(3). The two chelate rings around the metal, five- and six-membered, are not coplanar and form a dihedral angle of 42.0(1)°. While in the analogous compounds β-dichloro-(2-pyridinaldazine)zinc(II)[6] and dinitrato[bis(2-pyridylmethyl)-ketazine]copper(II)[7] all the M–N distances are similar, in $[ZnL^1Cl_2]$ the distances of the metal ion from the two pyridine nitrogens are practically the same [2.100(3) Å], but N(3) is remarkably farther away [2.339(3) Å] (Table 1). Probably this is due to the steric effect of the phenyls that pull the pyridine rings away and Zn^{II} with them. There are no remarkable differences in the bond distances of the ligand molecule, both respect to free L^1 and the literature complexes.

The reactivity of L^1 towards $CuCl_2$ is completely different. While methyl 2-pyridyl ketone azine reacts with $CuCl_2$ to give a binuclear complex,[7] with an equimolar amount of the same salt L^1 gives a green product identified by X-ray diffraction analysis as $[CuL^2{}_2Cl_2]$. Compound L^2 is obtained by aerial oxidation, catalysed by the copper(II) salt, of the phenyl 2-pyridyl ketone hydrazone derived from hydrolysis of the starting azine. It had been noted that 2-pyridyl ketone hydrazones suffer from aerial oxidation catalysed by various metal salts;[19] this property was used in the spectrofluorimetric determination of copper and in the determination of amino acids and proteins in a flow system,[20] but little is known about the co-ordination chemistry involved.[10,21]

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

$[ZnL^1Cl_2]$			
Zn–Cl(1)	2.299(1)	Zn–N(3)	2.339(3)
Zn–Cl(2)	2.247(2)	Zn–N(4)	2.100(3)
Zn–N(1)	2.100(3)		
N(3)–Zn–N(4)	71.8(1)	Cl(2)–Zn–N(1)	118.1(1)
N(1)–Zn–N(4)	119.9(1)	Cl(1)–Zn–N(4)	99.2(1)
N(1)–Zn–N(3)	75.9(1)	Cl(1)–Zn–N(3)	165.2(1)
Cl(2)–Zn–N(4)	109.0(1)	Cl(1)–Zn–N(1)	99.7(1)
Cl(2)–Zn–N(3)	86.5(1)	Cl(1)–Zn–Cl(2)	107.9(1)
$[CuL^2{}_2Cl_2]$			
Cu–Cl	2.230(2)	Cu–N(1)	2.007(4)
Cl–Cu–N(1)	90.7(1)		
CuL^3Cl_2			
Cu–Cl(1)	2.229(2)	Cu–N(1)	2.017(3)
Cu–Cl(2)	2.252(2)	Cu–N(2)	2.043(3)
N(1)–Cu–N(2)	79.8(1)	Cl(1)–Cu–N(2)	173.4(1)
Cl(2)–Cu–N(2)	92.1(1)	Cl(1)–Cu–N(1)	94.5(1)
Cl(2)–Cu–N(1)	172.0(1)	Cl(1)–Cu–Cl(2)	93.6(1)

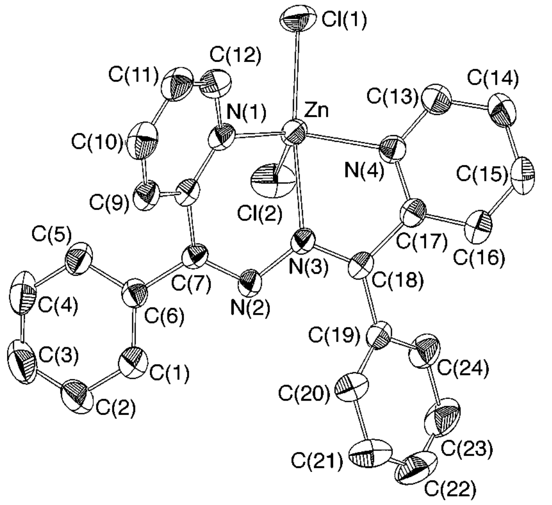

Fig. 3 An ORTEP diagram for $[ZnL^1Cl_2]$; thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted

The ORTEP drawing and the atom labelling scheme for $[CuL^2{}_2Cl_2]$ is given in Fig. 4, where symmetry-related atoms are not labelled. The crystallographic unit consists of half a copper atom, one ligand molecule and one chlorine atom. Since the space group *C*2/*c* has eight general positions, the four molecules per unit cell are constrained at special positions: the metal ion lies on a crystallographic inversion centre. The structure consists of well separated molecular units in which the Cu atom is co-ordinated to two N atoms from two ligand molecules and two chlorine anions in a typical *trans* square-planar environment. The metal atom does not form any other contacts less than 4 Å. The Cu, Cl(1), N(1) plane forms with the triazolo-[1,5-*a*]pyridine ring a dihedral angle of 77.5(1)° and with the

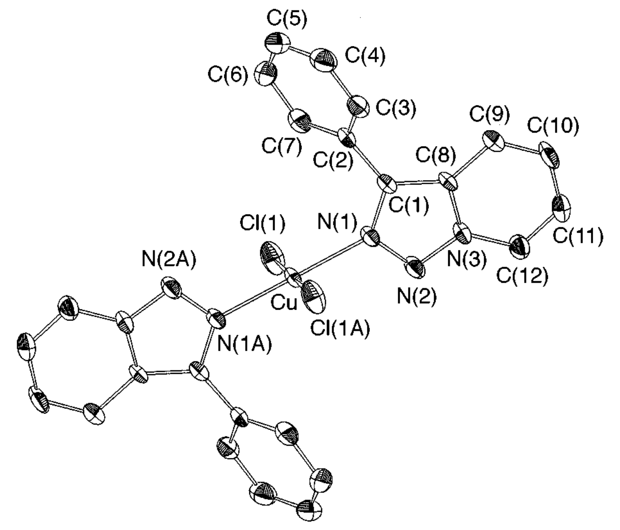

Fig. 4 An ORTEP diagram for [$CuL^2{}_2Cl_2$]; details as in Fig. 3

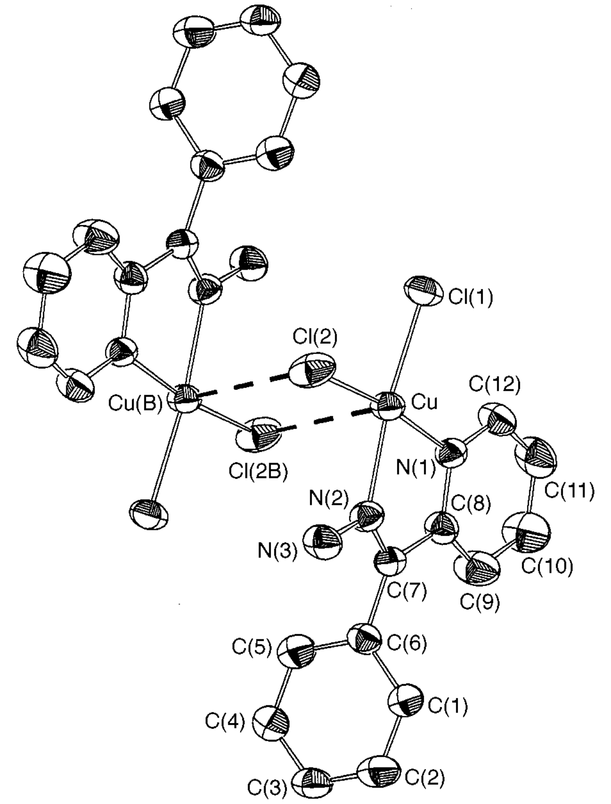

Fig. 5 An ORTEP diagram for the CuL^3Cl_2 binuclear unit showing the chloride bridge; details as in Fig. 3

phenyl ring an angle of 80.2(1)°. The bulky phenyl groups, which are perpendicular to this plane, prevent the [4 + 2] co-ordination found in similar compounds.[22]

From the direct reaction of phenyl 2-pyridyl ketone hydrazone (L^3) with $CuCl_2$ two products were obtained: a yellow-green microcrystalline powder together with deep green crystals of formula CuL^3Cl_2. An X-ray crystallographic analysis undertaken on CuL^3Cl_2 showed that the complex is built up by monomeric units, linked two by two through an elongated Cu···Cl contact (Fig. 5). The resulting geometry is distorted square pyramidal with N(1), N(2), Cl(1) and Cl(2) in the basal plane and the Cl(2) atom at $-x$, $-y$, $1 + z$ in the apical position [Cu···Cl(2B) 3.071(2) Å]. The ligand is bidentate through the pyridine and imine nitrogens, while N(3) does not participate in the co-ordination. The complex can be described in terms of two portions: the plane containing the pyridyl ring, the hydrazone arm, the copper(II) and the chlorine ions [maximum displacement 0.19 Å for N(3)], and the phenyl ring which forms a dihedral angle of 103.1(1)° with the former plane.

The second product seems to be a copper(I) complex of formula $CuL^2(Cl)\cdot 0.5H_2O$. In the IR spectrum there are no $\nu(NH_2)$ hydrazone bands, but on the contrary an absorption at 1629 cm^{-1} typical of the triazole moiety; the ^1H NMR spectrum, well resolved and without paramagnetic shift, confirms the oxidation of the hydrazone to triazole. As it is well known that the reversible change of oxidation state, *i.e.* $Cu^{II} \Longleftrightarrow Cu^{I}$, is linked to the catalytic function of copper, $CuL^2(Cl)\cdot 0.5H_2O$ can be seen, probably, as a step in the aerial oxidation of the 2-pyridyl ketone hydrazone by Cu^{II}. In an analogous way, from the reaction of pentane-2,4-dione dioxime with $CuCl_2\cdot 2H_2O$, *catena*-poly[(3,5-dimethylisoxazole)copper(I)-μ-dichloro][23] was isolated: the starting ligand, after aerial oxidation and cyclization, gives the copper(I) complex of the isoxazole derivative. The role of the copper ion is clearly crucial: a lot of complexes of 2-formyl- (Fe^{II}, Co^{II}, Ni^{II}),[24] 2-acetyl- and 2-benzoylpyridine (Co^{II}, Zn^{II})[25] hydrazones with various metal to ligand ratios have been reported, but the oxidation of the ligand was not observed.

Experimental

All reagents were of commercial quality used without further purification. Elemental analyses (C, H and N) were carried out on an automatic Carlo Erba CHNS-O EA1108 elemental analyser. Infrared spectra (4000–400 cm^{-1}) for KBr discs were recorded on a Nicolet 5PC FT-IR spectrometer, mass spectra on a Finnigan SSQ710 instrument, ^1H and ^{13}C NMR spectra on a Bruker ACX 300 instrument; chemical shifts are given in ppm referred to tetramethylsilane. Melting points were obtained with a Gallenkamp MFB-595 apparatus in open capillaries. Computations were carried out using SPARTAN[26] software, running on a UNIX workstation, IBM PowerPC 25T and DEC Alpha 255 computer with graphic processor.

X-Ray crystallography

Crystal data and relevant details concerning data collection and refinement for L^1 (**A** and **B** forms), [ZnL^1Cl_2], [$CuL^2{}_2Cl_2$] and $CuL^3(Cl)$ are summarized in Table 2. The data were collected at 293(2) K; no absorption correction was applied. The integrated intensities were measured using a modified version of the Lehmann and Larsen peak-profile analysis procedure.[27] The structures were solved by conventional direct methods (SHELXS 86[28] and SIR 92[29]) for **A**, **B** and the zinc(II) complex, and Patterson and Fourier techniques for both copper(II) complexes, and refined by full-matrix least-squares procedures, based on *F*. Anisotropic thermal parameters were assumed for all non-hydrogen atoms. All the hydrogen atoms were located from Fourier-difference maps and refined isotropically. The calculations were performed on GOULD POWERNODE 6040 and ENCORE91 computers, using SHELX 76,[30] PARST,[31] ORTEP[17] and PLUTO[32] programs.

CCDC reference number 186/840.

Syntheses

Compound L^1 (A and B forms). Hydrazine (99%, 0.26 cm^3) and a few drops of acetic acid were added to phenyl 2-pyridyl ketone (2 g) dissolved in methanol (40 cm^3); the solution was refluxed for *ca.* 5 h [the reaction was followed by TLC: SiO_2, hexane–ethyl acetate (1:3)]. On standing, at first white crystals (form **A**) of phenyl 2-pyridyl ketone azine separated and then yellow ones (form **B**). Crystals of **A** and **B** suitable for X-ray diffraction analysis were obtained by slow recrystallization from methanol. Overall yield 85% (**A**:**B**, 60:40; no attempt was made to optimize the yield of one of the two isomers) (Found: C, 79.98; H, 5.13; N, 15.30. $C_{24}H_{18}N_4$ requires C, 79.54; H, 5.01; N, 15.46%). Mass spectrum: *m*/*z* 362 (*M* + 1, 100%). Forms **A** and **B** have the same ^{13}C NMR spectrum ($CDCl_3$): δ 159.4,

Table 2 Crystal data and summary of intensity data collection and structure refinement

	A	**B**	[ZnL^{1}Cl$_2$]	[CuL$^2{}_2$Cl$_2$]	CuL^{3}Cl$_2$
Formula	$C_{24}H_{18}N_4$	$C_{24}H_{18}N_4$	$C_{24}H_{18}Cl_2N_4Zn$	$C_{24}H_{18}Cl_2CuN_6$	$C_{12}H_{11}Cl_2CuN_3$
M	362.43	362.43	498.72	524.90	331.69
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$
a/Å	21.685(8)	8.651(5)	11.240(3)	10.802(7)	9.112(3)
b/Å	5.657(3)	9.913(2)	14.966(3)	13.719(11)	9.058(3)
c/Å	15.450(6)	6.134(4)	13.562(3)	15.542(10)	9.195(3)
α/°		88.16(6)			66.95(4)
β/°	93.48(4)	83.48(4)	95.79(6)	105.35(6)	109.22(5)
γ/°		64.77(3)			103.74(4)
U/Å^3	1892(1)	472.7(4)	2269.7(9)	2221(3)	654.2(4)
Z	4	1	4	4	2
D_c/g cm^{-3}	1.272	1.273	1.459	1.570	1.684
μ/mm^{-1}	0.61	0.08	1.34	1.25	2.06
Diffractometer	Siemens AED	Siemens AED	Siemens AED	Philips PW 1100	Siemens AED
Scan mode	θ–2θ	θ–2θ	θ–2θ	θ–2θ	θ–2θ
Radiation, λ/Å	Cu-Kα, 1.541 78	Mo-Kα, 0.710 69	Mo-Kα, 0.710 69	Mo-Kα, 0.710 69	Mo-Kα, 0.710 69
Standard reflection	5 2 1	1 7 1	4 0 6	−4 6 2	4 4 2
Decay of standard	None	None	None	None	None
Reflections measured	1960	2024	3879	1304	2436
θ Range/°	3–70	3–30	3–24	3–24	3–27
Criterion for observation	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Reflections unique and observed	1687	1490	2857	1241	2341
No. parameters varied	163	163	352	187	207
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.0743	0.0423	0.0391	0.0452	0.0552
$R' = [\Sigma w(\Delta F^2)/\Sigma w F_o{}^2]^{\frac{1}{2}}$	0.1472	0.0635	0.0577	0.0615	0.0879
Minimum, maximum Δρ/e Å^{-3}	−0.30, 0.20	−0.19, 0.14	−0.87, 0.54	−0.28, 0.34	−0.22, 0.16

158.5, 158.1, 157.1, 155.9, 155.8, 154.3(5), 149.3, 149.2, 148.7, 136.5, 136.1, 135.9, 135.6, 135.5, 133.9, 130.0, 129.8, 129.6, 128.9, 128.3, 128.0, 127.9, 127.5, 127.4, 125.2, 124.6, 123.5, 123.4 and 123.0. **A**: m.p. 163 °C; main IR bands 1580m [ν(C=N)]; 1562m; 890s, 792m, 768m, 743m and 662m cm^{-1} (ring motions). **B**: m.p. 164 °C, main IR bands 1600m [ν(C=N)]; 1562m; 894s, 788m, 775m, 747m and 662m cm^{-1} (ring motions).

[ZnL^{1}Cl$_2$]. Compound L^1 (**A** or **B**) (0.1 g) was refluxed for 2 h with an equimolar amount of the zinc salt in methanol (30 cm^3). Slow evaporation of the solution gave orange crystals suitable for X-ray diffraction analysis, m.p. ≈270 °C (decomp.), yield 70% (Found: C, 57.74; H, 4.09; N, 11.21. $C_{24}H_{18}Cl_2N_4Zn$ requires C, 57.80; H, 3.64; N, 11.23%). Main IR band: 1584 cm^{-1} [ν(C=N)].

[CuL$^2{}_2$Cl$_2$]. When L^1 was treated with an equimolar amount of $CuCl_2$ under the same experimental conditions as above, a green powder together with a few crystals suitable for X-ray diffraction analysis were formed; the product was characterized and identified as [CuL$^2{}_2$Cl$_2$], m.p. 183 °C (decomp.), yield 55% (Found: C, 55.22; H, 3.81; N, 15.93. $C_{24}H_{18}Cl_2CuN_6$ requires C, 54.91; H, 3.43; N, 16.01%). Main IR bands: 1635 [ν(C=N)] and 794–693 cm^{-1} (ring motions).

Compound L^3. The hydrazone was prepared following the literature method,[27] m.p. 100.0–101.4 °C (lit., 99–100 °C). Mass spectrum: m/z 198 (M + 1, 100) and 181 (M − NH$_2$, 50%). Main IR bands: 3354, 3283, 3200 [ν(N–H)], 1589 [ν(C=N)] and 787–622 cm^{-1} (ring motions).

Reaction of L^3 with copper(II) chloride. Compound L^3 (0.1 g) was dissolved in ethanol (50 cm^3) with an equimolar amount of $CuCl_2\cdot H_2O$ and then the solution was refluxed for 2 h; on standing deep green crystals of CuL^{3}Cl$_2$, suitable for X-ray diffraction analysis, separated together with a yellow-green powder that was characterized as CuL^2(Cl)·0.5H$_2$O.

CuL^{3}Cl$_2$. M.p. 160–162 °C (decomp.), yield 40% (Found: C, 43.45; H, 3.31; N, 12.61. $C_{12}H_{11}Cl_2CuN_3$ requires C, 43.45; H, 3.34; N, 12.67%). Main IR bands: 3353 (br), 3264m [ν(N–H)], 1597m [ν(C=N)] and 789–680m cm^{-1} (ring motions).

CuL^2(Cl)·0.5H$_2$O. M.p. 197 °C (decomp.), yield 45% (Found: C, 47.55; H, 2.79; N, 13.80. $C_{12}H_{10}ClCuN_3O_{0.5}$ requires C, 47.53; H, 3.32; N, 13.86%). ^{1}H NMR [(CD$_3$)$_2$SO]: δ 7.24 (t, 1 H), 7.45–7.54 (m, 4 H), 8.02 (d, 2 H), 8.28 (d, 1 H) and 9.12 (d, 1 H). Main IR bands: 1629mw [ν(C=N)] and 780–681m cm^{-1} (ring motions).

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References

1 X. Xu, X. You, Z. Sun, X. Wang and H. Liu, *Acta Crystallogr., Sect. C*, 1994, **50**, 1169.

2 R. Bauer and Ch. O. Rupe, *Anal. Chem.*, 1971, **43**, 421.

3 G. Shiahuy Chen, J. K. Wilbur, Ch. L. Barnes and R. Glaser, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2311.

4 V. L. Goedken, Y. Park, S. M. Peng and J. M. Norris, *J. Am. Chem. Soc.*, 1974, **96**, 7693; C. Thilgen and F. Vögtle, *Chem. Ber.*, 1991, **124**, 671; Th. W. Bell and A. T. Papoulis, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 749.

5 P. Espinet, J. Etxebarria, M. Marcos, J. Pérez, A. Remon and J. L. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1065.

6 H. Warren Smith, *Acta Crystallogr., Sect. B*, 1975, **31**, 2701.

7 Ch. J. O'Connor, R. J. Romananch, D. M. Robertson, E. E. Eduok and F. R. Fronczek, *Inorg. Chem.*, 1983, **22**, 449.

8 W. J. Stratton, *Inorg. Chem.*, 1970, **9**, 517 and refs. therein; P. D. W. Boyd, M. Gerloch and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1974, 1097.

9 I. Bertini, Ch. Owens, C. Luchinat and R. S. Drago, *J. Am. Chem. Soc.*, 1987, **109**, 5208.

10 L. P. Battaglia, M. Carcelli, F. Ferraro, L. Mavilla, C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1994, 2651.

11 C. Amari, C. Pelizzi, G. Predieri, S. Destri and W. Porzio, *Synth. Met.*, 1995, **72**, 7.

12 J. Bernstein and A. T. Hagher, *J. Am. Chem. Soc.*, 1978, **100**, 673.

13 G. S. Chen, M. Anthamatten, Ch. L. Barnes and R. Glaser, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1081.

14 E. C. K. Lai, D. Mackay, N. J. Taylor and K. N. Watson, *Can. J. Chem.*, 1988, **66**, 2839.

15 I. Fleming and J. Harley-Mason, *J. Chem. Soc.*, 1961, 5560.

16 T. Ishida, M. Inoue, K. Nasu and T. Kurihara, *Acta Crystallogr.*, *Sect. C*, 1983, **39**, 470.
17 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
18 R. Glaser, G. Shiahuy Chen and Ch. Barnes, *J. Org. Chem.*, 1993, **58**, 7446.
19 F. Grases, F. Garcia-Sanchez and M. Valcarcel, *Anal. Chim. Acta*, 1981, **125**, 21; H. Mori, K. Sakamoto, S. Mashito, Y. Matsouka, M. Matsubayashi and K. Sakai, *Chem. Pharm. Bull.*, 1993, **41**, 1944.
20 H. Mori, K. Sakai, K. Yamashina, S. Hirata and K. Horie, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 3634.
21 E. Escrivà, J. Server-Carrió, L. Lezama, J. V. Folgado, J. L. Pizarro, R. Ballesteros and B. Abarca, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2033.
22 G. Valle, R. Ettorre and V. Peruzzo, *Acta Crystallogr.*, *Sect. C*, 1995, **51**, 1293.
23 K. J. Oliver, T. N. Waters, D. F. Cook and C. E. F. Rickard, *Inorg. Chim. Acta*, 1977, **24**, 85.
24 R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, 1956, **78**, 6016.
25 D. Demertzi and D. Nicholls, *Inorg. Chim. Acta.*, 1983, **73**, 37.
26 *SPARTAN User's guide*, Wavefunction Inc., Irvine, CA, 1996.
27 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
28 G. M. Sheldrick, SHELXS 86, Program for the solution of crystal structures, University of Göttingen, 1985.
29 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, G. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
30 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
31 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
32 W. D. S. Motherwell and W. Clegg, PLUTO, Program for plotting molecular and crystal structure, University of Cambridge, 1976.

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