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Cu(II) complexes with pyrazole-derived ligands. Crystal structure of {[diaquanitrato(3-phenyl-5-(2-pyridyl)pyrazole)]copper(II)} nitrate

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Abstract

Reaction of the ligands 3-phenyl-5-(2-pyridyl)pyrazole (HL^0) and 3-phenyl-5-(6-methyl-(2-pyridyl))pyrazole (HL^1) with $Cu(NO_3)_2{\cdot}3H_2O$ and $CuX_2{\cdot}xH_2O$ (X = Cl, Br) gives complexes with stoichiometry $Cu(HL^0)_2X_2{\cdot}xH_2O$, $Cu(HL^1)_2X_2{\cdot}EtOH$, $Cu(HL)X_2$, $Cu(HL)_2(NO_3)_2{\cdot}xH_2O$ ($HL = HL^0$, HL^1) and $Cu(HL^0)(NO_3)_2{\cdot}2H_2O$. The new complexes were characterised by elemental analyses, conductivity measurements and infrared and electronic spectroscopy. The crystal and molecular structure of $[Cu(HL^0)(NO_3)(H_2O)_2](NO_3)$ consists of discrete cations and NO_3^- anions linked by hydrogen bonds. The cation complex $[Cu(HL^0)(NO_3)(H_2O)_2]^+$ contains a copper(II) with a distorted tetragonal pyramid geometry ($\tau = 0.094$), with a H_2O ligand occupying the apical site. The penta-coordinated metal atom is bonded to one pyridinic nitrogen, one pyrazolic nitrogen, one nitrate and two water molecules. The ligand HL^0 is not completely planar. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Copper complexes; Pyrazole complexes; Crystal structures

1. Introduction

Research on the coordination chemistry of pyrazole-derived ligands has progressed very rapidly over the last two decades. Mukherjee published an extensive review in 2000 [1], which complements those presented by La Monica and Ardizzoia in 1997 [2], and by Trofimenko in 1986 and 1993 [3,4].

Bidentate and tridentate nitrogen heterocyclic compounds containing six-membered rings such as 2,2′-bipyridine, 1,10-phenantroline and 2,2′:6′,2″-terpyridine have been extensively used in transition metal chemistry [5–7]. The incorporation of pyrazole groups in the design of new ligands allows both the electronic and steric control of the properties of metal complexes. A six-membered heterocycle like pyridine and a five-membered heterocycle like pyrazole are thus directly linked in a single ligand system [8], because the electronic communication between these two heterocycles can be avoided.

The bidentate ligands 3-(2-pyridyl)pyrazole [9–11], 3-methyl-5-(2-pyridyl)pyrazole [12] and 3-*tert*-butyl-5-(2-pyridyl)pyrazole [12] have been described elsewhere, revealing a remarkable coordination chemistry [12–21].

Our group has reported the preparation of the ligands 3,5-bis(2-pyridyl)pyrazole (HL′), 3-(6-methyl-2-pyridyl)-5-(2-pyridyl)pyrazole (HL″) and 3,5-bis-2-(6-methylpyridyl)pyrazole (HL‴) and studied their reactivity with the divalent metal ions Ni(II), Co(II), Zn(II) and Cu(II) [22–25]. In 1995, Munakata et al. [26] described three HL′ complexes, two of Ag(I) and one of Cu(II).

We have recently reported the synthesis of the ligands 3-phenyl-5-(2-pyridyl) pyrazole (HL^0) and 3-phenyl-5-(6-methyl-(2-pyridyl))pyrazole (HL^1) (Fig. 1) and that of several Co(II), Pd(II) and Ni(II) complexes [27–29].

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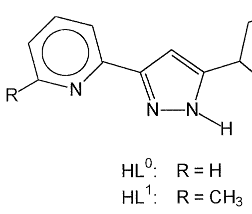

Fig. 1. Pyrazole-derived ligands HL^0 and HL^1.

Here, we study the synthesis and structural determination of the Cu(II) complexes of the ligands HL^0 and HL^1. The crystal structure of $[Cu(HL^0)(NO_3)(H_2O)_2](NO_3)$ is described and compared with that of closely related structures.

2. Experimental

2.1. General methods

Preparations were performed under nitrogen using usual Schlenk techniques. All reagents were commercial grade materials and were used without further purification. All solvents (ethanol, acetonitrile and ether) were previously deoxygenated in a vacuum line.

Analysis (C, H, N) were performed in our analytical laboratory on a Perkin–Elmer 240-B instrument. Conductivity measurements were performed at room temperature (r.t.) in 10^{-3} M in DMF and 10^{-3} M in DMSO solutions employing a Radiometer CDM-3 conductimeter.

Infrared spectra were recorded from KBr disks or Nujol films on a Perkin–Elmer 2000 spectrometer in the region 4000–100 cm^{-1}. UV–Vis electronic spectra between 750 and 350 nm, in DMF solution, were run on a Kontron-Uvikon 860 and in solid state (KBr pellets, diffuse reflectance) on a Kontron-Tegimenta CH-6343 Rotkreuz AG. NIR electronic spectra between 1750 and 750 nm, in DMF solution, were run on a NIRSystem.

2.2. Synthesis of ligands

The compounds 3-phenyl-5-(2-pyridyl)pyrazole (HL^0) and 3-phenyl-5-(6-methyl-(2-pyridyl))pyrazole (HL^1) were synthesised as previously reported [27] (Fig. 1).

2.3. Synthesis of the metal complexes

2.3.1. Complexes $Cu(HL^0)_2X_2 \cdot xH_2O$ where $X = Cl$, $x = 2$ (**1**), $X = Br$, $x = 1$ (**2**) and $Cu(HL^1)_2X_2 \cdot EtOH$ where $X = Cl$ (**3**) and $X = Br$ (**4**)

The appropriate metal salt (0.22 mmol: $CuCl_2 \cdot 2H_2O$, 0.037 g; $CuBr_2$, 0.049 g) dissolved in ethanol (10 ml) was added to a solution of the ligand (0.45 mmol: HL^0, 0.10 g; HL^1, 0.11 g) in ethanol (10 ml). The resulting solution was stirred at r.t. for 20 h; crystalline solids were obtained which were filtered off and dried in vacuum, washed with ethanol–acetonitrile (50%) and vacuum dried. The same products (stoichiometry and yield) were obtained when a 1:1 Cu/HL ratio was used.

1: IR (KBr, cm^{-1}): ν(N–H) 3205; $\nu(C–H)_{ar}$ 3011; ν(C=C), ν(C=N) 1614, 1574; $\delta(C–H)_{OOP}$ 788, 762; ν(Cu–N) 410; ν(Cu–Cl) 320, 296; ν(Cu–N) 258. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.31×10^{-3} M): 811(166). UV–Vis: λ (nm) (KBr): 820, 490.

2: IR (KBr, cm^{-1}): ν(N–H) 3198; $\nu(C–H)_{ar}$ 3053; ν(C=C), ν(C=N) 1612, 1572; $\delta(C–H)_{OOP}$ 788, ν(Cu–N) 408; ν(Cu–Br) 292, 268; ν(Cu–N) 258. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.16×10^{-3} M): 806(165). UV–Vis: λ (nm) (KBr): 818, 453.

3: IR (KBr, cm^{-1}): ν(N–H) 3109; $\nu(C–H)_{ar}$ 3061; ν(C=C), ν(C=N) 1616, 1578; $\delta(C–H)_{OOP}$ 793, 764; ν(Cu–N) 531; ν(Cu–Cl) 281, 266; ν(Cu–N) 226. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.19×10^{-3} M): 874(201). UV–Vis: λ (nm) (KBr): 820, 460.

4: IR (KBr, cm^{-1}): ν(N–H) 3108; $\nu(C–H)_{ar}$ 3059; ν(C=C), ν(C=N) 1614, 1576; $\delta(C–H)_{OOP}$ 794, 768; ν(Cu–N) 530; ν(Cu–Br) 278, 266; ν(Cu–N) 228. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.08×10^{-3} M): 874(300). UV–Vis: λ (nm) (KBr): 820, 500.

2.3.2. Complexes $Cu(HL)X_2$ where $HL = HL^0$, $X = Cl$ (**5**), $HL = HL^0$, $X = Br$ (**6**) $HL = HL^1$, $X = Cl$ (**7**), and $HL = HL^1$, $X = Br$ (**8**)

To a Schlenk flask containing deoxygenated warm ethanol (20 ml) was added, in this order HL (0.45 mmol: HL^0, 0.10 g; HL^1 0.11 g) and $CuX_2 \cdot xH_2O$ (0.90 mmol). The resulting solution was stirred at r.t. for 24 h. Crystalline solids were obtained, which were filtered off, washed with ethanol and ether and vacuum dried.

5: IR (KBr, cm^{-1}): ν(N–H) 3129; $\nu(C–H)_{ar}$ 3058; ν(C=C), ν(C=N) 1615, 1571; $\delta(C–H)_{OOP}$ 776, 762; ν(Cu–N) 414; ν(Cu–Cl) 320, 273; ν(Cu–N) 248. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.70×10^{-3} M): 822(113). UV–Vis: λ (nm) (KBr): 734, 490.

6: IR (KBr, cm^{-1}): ν(N–H) 3225; $\nu(C–H)_{ar}$ 3091; ν(C=C), ν(C=N) 1615, 1563; $\delta(C–H)_{OOP}$ 778, 763; ν(Cu–N) 410; ν(Cu–Br) 306, 269; ν(Cu–N) 262. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.35×10^{-3} M): 848(178). UV–Vis: λ (nm) (KBr): 720, 516.

7: IR (KBr, cm^{-1}): ν(N–H) 3126; $\nu(C–H)_{ar}$ 3067; ν(C=C), ν(C=N) 1615, 1564; $\delta(C–H)_{OOP}$ 799, 771; ν(Cu–N) 530; ν(Cu–Cl) 276, 254; ν(Cu–N) 232. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.08×10^{-3} M): 970(156). UV–Vis: λ (nm) (KBr): 780, 550.

8: IR (KBr, cm^{-1}): ν(N–H) 3233; $\nu(C–H)_{ar}$ 3060; ν(C=C), ν(C=N) 1614, 1562; $\delta(C–H)_{OOP}$ 795, 762; ν(Cu–N) 530; ν(Cu–Br) 278, 266; ν(Cu–N) 232. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.09×10^{-3} M): 900(158). UV–Vis: λ (nm) (KBr): 797, 535.

Table 1
Physical and analytical data for the complexes

Compound	Colour	Yield (%)	Analysis [a]			Conductivity [d] (Ω^{-1} cm^2 mol^{-1})
			C (%)	N (%)	H (%)	
$Cu(HL^0)_2Cl_2{\cdot}2H_2O$ (**1**)	green	41	(54.9)	(13.7)	(4.3)	27 [b]
			54.3	13.7	4.1	45 [c]
$Cu(HL^0)_2Br_2{\cdot}H_2O$ (**2**)	green	76	(49.2)	(12.3)	(3.5)	53 [b]
			48.9	12.1	3.6	62 [c]
$Cu(HL^1)_2Cl_2{\cdot}EtOH$ (**3**)	green	92	(59.0)	(12.9)	(4.9)	54 [b]
			58.7	12.7	4.7	50 [c]
$Cu(HL^1)_2Br_2{\cdot}EtOH$ (**4**)	green	95	(51.9)	(11.4)	(4.4)	69 [b]
			51.6	11.2	4.3	68 [c]
$Cu(HL^0)Cl_2$ (**5**)	green	80	(47.3)	(11.8)	(3.1)	24 [b]
			47.2	11.8	3.1	52 [c]
$Cu(HL^0)Br_2$ (**6**)	brown	80	(37.8)	(9.4)	(2.5)	47 [b]
			37.8	9.4	2.4	49 [c]
$Cu(HL^1)Cl_2$ (**7**)	brown	95	(48.7)	(11.4)	(3.5)	38 [b]
			48.7	11.2	3.6	56 [c]
$Cu(HL^1)Br_2$ (**8**)	brown	94	(39.3)	(9.2)	(2.9)	86 [b]
			39.6	8.9	2.9	55 [c]
$Cu(HL^0)_2(NO_3)_2$ (**9**)	green	85	(53.3)	(17.8)	(3.5)	94 [b]
			53.1	17.4	3.6	58 [c]
$Cu(HL^1)_2(NO_3)_2{\cdot}H_2O$ (**10**)	green	40	(53.3)	(16.6)	(4.2)	125 [b]
			53.1	16.2	4.3	57 [c]
$Cu(HL^0)(NO_3)_2{\cdot}2H_2O$ (**11**)	green	58	(37.8)	(15.7)	(3.4)	95 [b]
			37.3	15.6	3.2	68 [c]

[a] Calculated analytical values are given in parentheses.

[b] 10^{-3} M in DMF.

[c] 10^{-3} M in DMSO.

[d] The reported values for 1:1 and 1:2 electrolytes in DMF are 65–90 and 130–170 Ω^{-1} cm^2 mol^{-1} conductivity, respectively, and in DMSO, the values for 1:1 electrolytes are 50–70 Ω^{-1} cm^2 mol^{-1} [32–34].

2.3.3. Complexes $Cu(HL)_2(NO_3)_2{\cdot}xH_2O$ where $HL = HL^0$, $x = 0$ (9), $HL = HL^1$, $x = 1$ (10)

The appropriate ligand (0.45 mmol: HL^0, 010 g; HL^1, 0.11 g) was added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.22 mmol, 0.053 g) in ethanol (10 ml). Upon addition no appreciable change in colour was observed, but after 1 h crystalline solids were obtained, which were filtered off and dried in vacuum.

9: IR (KBr, cm^{-1}): ν(N–H) 3121; ν(C–H)$_{ar}$ 3065; ν(C=C), ν(C=N) 1610, 1575; δ(C–H)$_{OOP}$ 786, 763; ν(Cu–N) 412; ν(Cu–O) 272, ν(Cu–N) 244. IR (Nujol, cm^{-1}): $\nu_1 + \nu_3(NO_3)$ 1770, 1749, 1735, 1715. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.10×10^{-3} M): 616(96). UV–Vis: λ (nm) (KBr): 767, 480.

10: IR (KBr, cm^{-1}): ν(N–H) 3105; ν(C–H)$_{ar}$ 3064; ν(C=C), ν(C=N) 1616, 1575; δ(C–H)$_{OOP}$ 798, 767; ν(Cu–N) 439; ν(Cu–O) 278, ν(Cu–N) 248. IR (Nujol, cm^{-1}): $\nu_1 + \nu_3(NO_3)$ 1767, 1763, 1750, 1746. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.18×10^{-3} M): 844(82). UV–Vis: λ (nm) (KBr): 820, 500.

2.3.4. Complex $Cu(HL^0)(NO_3)_2{\cdot}2H_2O$ (11)

To a Schlenk flask containing deoxygenated warm ethanol (20 ml) was added, in this order, HL^0 (0.45 mmol, 0.10 g) and $Cu(NO_3)_2{\cdot}3H_2O$ (0.45 mmol, 0.11 g). The resulting solution was stirred at r.t. for 5 h and concentrated on a vacuum line to one-fifth of the initial volume. After standing at r.t. for 2 h, a crystalline solid was obtained, which was filtered off and dried in vacuum, washed with ethanol and vacuum dried.

11: IR (KBr, cm^{-1}): ν(N–H) 3212; ν(C–H)$_{ar}$ 3096; ν(C=C), ν(C=N) 1616, 1573; δ(C–H)$_{OOP}$ 787, 763; ν(Cu–N) 417; ν(Cu–O) 278, ν(Cu–N) 250. IR (Nujol, cm^{-1}): $\nu_1 + \nu_3(NO_3)$ 1767, 1750, 1734, 1717. UV–Vis: $\lambda(\varepsilon)$ (nm) (DMF 1.22×10^{-3} M): 646(91). UV–Vis: λ (nm) (KBr): 720, 488.

Table 1 shows other analytical and physical data for all complexes.

2.4. X-ray crystal structure analysis

Suitable crystals for X-ray diffraction experiments of compound $[Cu(HL^0)(NO_3)(H_2O)_2](NO_3)$ (**11**) were obtained by crystallisation from an acetonitrile solution. One of them was mounted on an Enraf–Nonius CAD4 diffractometer. Intensities were collected using the ω–2θ scan mode to a $2\theta_{max} = 50°$. Graphite monochromated Mo Kα radiation was used. The structure was solved by direct methods (SHELXS-86) [30] and refined by full-matrix least-squares methods on F^2 for all reflections (SHELXL-97) [31]. The non-coordinated nitrate group is disordered. Two oxygen sets have been included with sof 0.6/0.4. The final $R(F)$ and $R_W(F^2)$ values as well as the number of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 2. The weight was $w^{-1} = \sigma^2(F_o^2) + (0.0561P)^2 + 0.1067P$ where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

3.1. Synthesis and spectroscopic properties of the complexes

The complexes $Cu(HL)_2X_2$ and $Cu(HL)X_2$ (X = Cl, Br) were obtained by reacting the appropriate metal salt with the corresponding pyrazole ligand in a M/L ratio of 1:2 or 1:1, respectively. Analogously, the complexes $Cu(HL)_2(NO_3)_2$ and $Cu(HL^0)(NO_3)_2$ were obtained when the M/L ratio was 1:2 and 1:1 stoichiometry, respectively. We failed to isolate the complex $Cu(HL^1)(NO_3)_2$.

The conductivity measurements of the complexes are shown in Table 1. For nitrate complexes, the electrolyte nature depends on the solvent. Conductivity in DMF ranged from 94 to 125 Ω^{-1} cm^2 mol^{-1}, i.e. between the values of electrolytes 1:1 and 1:2, whereas conductivity in DMSO ranged from 57 to 68 Ω^{-1} cm^2 mol^{-1}, which is consistent with the value of electrolyte 1:1. For the complexes of formula $Cu(HL)_2X_2$ and $Cu(HL)X_2$, the conductivity in DMF and DMSO is high enough to assess the non-coordinated nature of the halide anion.

Table 2
Crystal data and structure refinement of **11**

Compound	$[Cu(HL^0)(NO_3)(H_2O)_2](NO_3)$
Empirical formula	$C_{14}H_{15}CuN_5O_8$
Formula weight	444.85
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	8.349(3)
b (Å)	10.3623(10)
c (Å)	10.6886(7)
α (°)	66.516(8)
β (°)	88.116(14)
γ (°)	88.979(14)
V (Å^3)	847.7(3)
Z	2
D_{calc} (Mg m^{-3})	1.743
Absorption coefficient (mm^{-1})	1.347
Crystal size (mm)	$0.50 \times 0.20 \times 0.10$
Unique data/restraints/parameters	2974/20/292
R indices [$I > 2\sigma(I)$]	$R(F) = 0.029$, $R_w(F^2) = 0.079$
R indices (all data)	$R(F) = 0.033$, $R_w(F^2) = 0.080$
Goodness-of-fit on F^2	1.077
Largest difference peak and hole (e Å^{-3})	0.37 and −0.40

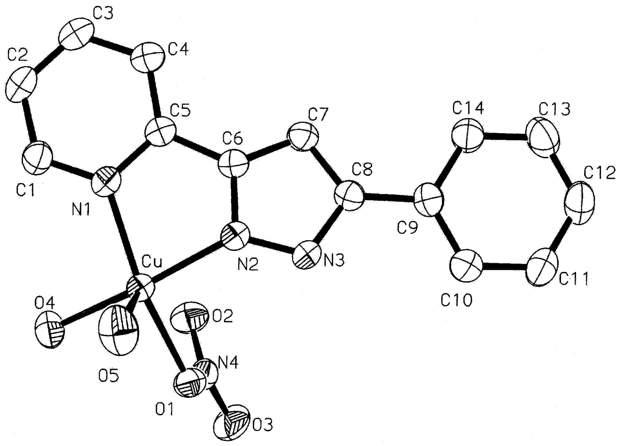

Fig. 2. An ORTEP view of the structure of the cation of **11**. The displacement ellipsoids enclose 50% probability.

The IR spectra of the complexes containing the nitrate anion, measured in the 1800–1600 cm^{-1} region, allowed us to determine the coordination mode of the NO_3^- anion. Lever and Montovani [35] studied the IR absorptions of the NO_3^- group in this region for various coordinations. The complexes $Cu(HL^0)_2(NO_3)_2$ (**9**), $Cu(HL^1)_2(NO_3)_2 \cdot H_2O$ (**10**) and $Cu(HL^0)(NO_3)_2 \cdot 2H_2O$ (**11**) show a complicated spectrum in this region, which is consistent with the presence of both ionic and coordinated NO_3^- groups, confirmed in the case of complex **11** by X-ray diffraction.

The IR spectra of halide complexes in the region 400–100 cm^{-1} were also measured. The complexes $Cu(HL)Cl_2$ and $Cu(HL)_2Cl_2$ display two well-defined ν(Cu–Cl) bands at 320–254 and 320–266 cm^{-1}, respectively. The bromide derivatives $Cu(HL)Br_2$ and $Cu(HL)_2Br_2$ show two bands ν(Cu–Br) at 306–266 and 292–266 cm^{-1}, respectively. The ν(Cu–N) absorptions appear in the range 531–226 cm^{-1}, in agreement with available data [36–39].

Electronic spectra for the synthesised complexes were measured in DMF, and in KBr pellets (diffuse reflectance).

The spectra of Cu(II) compounds in DMF solution show one band in the NIR or visible regions, 970–616 nm ($\varepsilon = 82$–300 mol^{-1} cm^{-1} l). Electronic spectra using diffuse reflectance methods show an additional band at 550–453 nm. These results did not allow us to infer the geometry of the metal centre [40–43].

3.2. Crystal structure of $[Cu(HL^0)(NO_3)(H_2O)_2](NO_3)$

The molecular structure of the complex (Fig. 2) consists of discrete $[Cu(HL^0)(NO_3)(H_2O)_2]^+$ cations

Table 3
Selected bond lengths (Å) and bond angles (°) of **11**

Bond lengths			
Cu–O5(H_2O)	2.1543(19)		
Cu–O4(H_2O)	1.9772(17)		
Cu–O1(NO_3)	2.0290(15)		
Cu–N2(pz)	1.9722(18)		
Cu–N1(py)	2.0191(18)		
Bond angles			
O4–Cu–O5	92.09(8)	O1–Cu–N1	161.88(7)
O4–Cu–O1	88.63(7)	O4–Cu–N2	167.55(8)
O5–Cu–O1	91.88(8)	O5–Cu–N2	100.29(8)
O4–Cu–N1	95.07(8)	O1–Cu–N2	92.22(7)
O5–Cu–N1	105.67(8)	N2–Cu–N1	80.43(7)

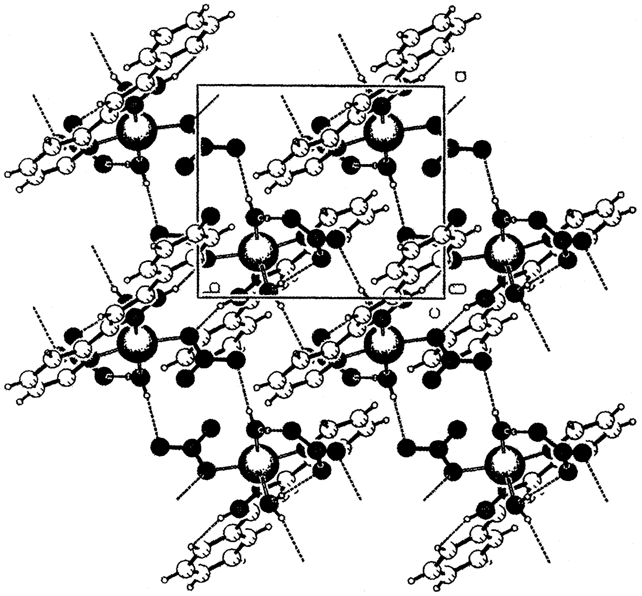

Fig. 3. A parallel view of the infinite 2D-lattice parallel to (001) plane formed by the different units of [Cu(HL^0)(NO_3)(H_2O)$_2$](NO_3) bonded by hydrogen bonds.

and NO_3^- anions. The cation complex is mononuclear. Table 3 lists selected bond distances and angles.

In the cation, the metal atom is coordinated to one HL^0 ligand, via one pyrazole nitrogen and one pyridine nitrogen, to one NO_3^- anion and to two H_2O molecules. HL^0 behaves as a bidentate ligand and uses only two of their three donor nitrogen atoms, forming a five-membered metallocycle.

The coordination around Cu is a distorted square pyramid. The trigonality index is $\tau = 0.094$ [44].

A H_2O ligand occupies the apical site [Cu–O5 = 2.1543(19) Å] whereas the Cu–O4 distance is 1.9772(17) Å (in basal position). These values are similar to those reported for other examples of Cu–H_2O bond distances [45,46].

The Cu–O1(NO_3) bond distance is 2.0290(15) Å, comparable to the Cu–O(NO_3) distance in other copper(II) complexes in which the metal is coordinated by a terminal nitrate 33 [47]. The other oxygen of this NO_3^-, O2, is close to copper by 2.6121(17) Å. If this distance is long enough to be considered a Cu–O interaction, the coordination polyhedron around Cu is a highly distorted octahedral.

Table 4
Hydrogen-bond parameters (Å, °) of **11**

	D–H	A···H	D···A	D–H···A
N3–H3···O1^{i} [a]	0.86	2.15	2.959(3)	156
O4–H42···O3^{ii} [b]	0.77(2)	2.29(2)	3.048(3)	168(2)
O4–H41···O71^{iii} [b]	0.77(2)	1.97(2)	2.729(7)	171(2)
O5–H52···O81^{iii} [b]	0.81(3)	2.05(3)	2.827(5)	161(3)
O5–H51···O61^{iv} [b]	0.80(4)	2.24(3)	2.962(8)	150(3)

(i) $-x, -y+2, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $x, y, z+1$; (iv) $-x, -y+1, -z+1$.

[a] N–H distances have been fixed.

[b] The non-coordinated nitrate is disordered. Only the main component of disorder is presented here.

The bond distance of Cu–Npy is clearly longer than that of Cu–Npz. Both bond distances are consistent with previously described values (1.996–2.092 Å) [24,26,45,46] and (1.929–2.056 Å) [24,26,46], respectively.

The bite angle of N1–Cu–N2, 80.4(8)°, is similar to that of tetranuclear copper(II) compounds with the related ligand HL′: 79.8(2)° [24], 80.3(2)° [26] and to that of other complexes with the ligands HL^0 and HL^1: 75.3–80.2° [27–29].

The ligand HL^0 is not completely planar. The pyridyl and phenyl groups are slightly twisted with respect to the pyrazole. The angles between rings are: py–pz 5.79(7)°, py–ph 2.51(6)° and pz–ph 5.65(9)° in this complex. These values are lower than the other published data [27–29].

Cations are linked by hydrogen bonding, yielding infinite chains parallel to the crystallographic vector *a*.

Each cation is bonded to two neighbours, each one of them is related with it by an inversion centre.

Two N3–H···O1 (coordinated nitrate) hydrogen bonds are established with one neighbour and two O (water) O4–H···O3 (coordinated nitrate) hydrogen bonds are established with the other.

The chains and the non-coordinated nitrate are also bonded by (water) O–H···O (nitrate) hydrogen bonds, yielding an infinite 2D-lattice parallel to the (001) plane (Fig. 3, Table 4).

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 157492 for compound **11**.

Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] R. Mukherjee, Coord. Chem. Rev. 203 (2000) 151.
[2] G. La Monica, G.A. Ardizzoia, Prog. Inorg. Chem. 46 (1997) 151.
[3] S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115.
[4] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[5] W.R. McWhinnie, J.D. Miller, Adv. Inorg. Chem. Radiochem. 12 (1969) 135.
[6] S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842.
[7] K. Niedenzu, S. Trofimenko, Top. Curr. Chem. 131 (1986) 1.
[8] E.C. Constable, P.J. Steel, Coord. Chem. Rev. 93 (1989) 205.
[9] A.J. Amoroso, A.M. Cargill Thompson, J.C. Jeffrey, P.L. Jones, J.A. McCleverty, M.D. Ward, J. Chem. Soc., Chem. Commun. (1994) 2751.
[10] H. Brunner, T. Scheck, Chem. Ber. 125 (1992) 701.
[11] Y. Lin, S.A. Lang, J. Heterocycl. Chem. 14 (1977) 345.
[12] A. Satake, T. Nakata, J. Am. Chem. Soc. 120 (1998) 10391.
[13] W.R. Thiel, M. Angstl, T. Priermeir, Chem. Ber. 127 (1994) 2373.
[14] J.C. Jeffrey, P.L. Jones, K.L.V. Mann, E. Psillakis, J.A. McCleverty, M.D. Ward, C.M. White, Chem. Commun. (1997) 175.
[15] P.L. Jones, J.C. Jeffrey, J.A. McCleverty, M.D. Ward, Polyhedron 16 (1997) 1567.
[16] K. Singh, J.R. Long, P.J. Stavropoulos, J. Am. Chem. Soc. 119 (1997) 4618.
[17] M.H.W. Lam, S.T.V. Cheung, K.M. Fung, W.T. Wong, Inorg. Chem. 36 (1997) 4618.
[18] E. Psillakis, J.C. Jeffrey, J.A. McCleverty, M.D. Ward, Chem. Commun. (1997) 1965.
[19] M.D. Ward, J.S. Fleming, E. Psillakis, J.C. Jeffrey, J.A. McCleverty, Acta Crystallogr., Sect. C 54 (1998) 609.
[20] K.L.V. Mann, E. Psillakis, J.C. Jeffrey, L.H. Rees, N.M. Harden, J.A. McCleverty, M.D. Ward, D. Gatteschi, F. Totti, F.E. Mabbs, E.J.L. McInnes, P.C. Reidi, G.M. Smith, J. Chem. Soc., Dalton Trans. (1999) 338.
[21] L.S. Harimanow, K.H. Sugiyarto, D.C. Craig, M.L. Scudder, H.A. Goodwin, Aust. J. Chem. 52 (1999) 109.
[22] J. Casabó, J. Pons, K. Siddiqi, F. Teixidor, E. Molins, C. Miravitlles, J. Chem. Soc., Dalton Trans. (1989) 1401.
[23] J. Pons, X. López, E. Benet, J. Casabó, F. Teixidor, F.J. Sánchez, Polyhedron 9 (1990) 2839.
[24] J. Pons, X. López, J. Casabó, F. Teixidor, A. Caubet, J. Rius, C. Miravitlles, Inorg. Chim. Acta 195 (1992) 61.
[25] J. Pons, F.J. Sánchez, A. Labarta, J. Casabó, F. Teixidor, A. Caubet, Inorg. Chim. Acta 208 (1993) 167.
[26] M. Munakata, L.P. Wu, M. Yamamoto, T. Kurodasowa, M. Maekawa, S. Kawata, S. Kitagawa, J. Chem. Soc., Dalton Trans. (1995) 4099.
[27] A. Chadghan, J. Pons, A. Caubet, J. Casabó, J. Ros, A. Alvarez-Larena, J.F. Piniella, Polyhedron 19 (2000) 855.
[28] J. Pons, A. Chadghan, J. Casabó, A. Alvarez-Larena, J.F. Piniella, J. Ros, Inorg. Chem. Commun. 3 (2000) 296.
[29] J. Pons, A. Chadghan, J. Casabó, A. Alvarez-Larena, J.F. Piniella, X. Solans, M. Font-Bardia, J. Ros, Polyhedron 20 (2001) 1029.
[30] G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Determination, University of Göttingen, Germany, 1986.
[31] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[32] P.J. Koningsbruggen, E. Müller, G.J. Haasnoot, J. Reedjick, Inorg. Chim. Acta 208 (1993) 37.
[33] L.K. Thompson, F.L. Lee, E.J. Gabe, Inorg. Chem. 27 (1988) 39.
[34] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.
[35] A.B.P. Lever, E. Montovani, Can. J. Chem. 49 (1971) 1957.
[36] N.S. Gill, H.J. Kingdon, Aust. J. Chem. 19 (1966) 2197.
[37] W.R. Whinnie, J. Inorg. Nucl. Chem. 27 (1965) 2573.
[38] J. Sletten, A. Sorensen, M. Julve, Y. Journaux, Inorg. Chem. 29 (1990) 5054.
[39] L.K. Thompson, A.W. Hanson, B.S. Ramaswamy, Inorg. Chem. 23 (1984) 2459.
[40] D. Sutton, Electronic Spectra of Transition Metal Complexes, McGraw-Hill, London, 1975.
[41] G. Murphy, P. Nagle, B. Murphy, B. Harhaway, J. Chem. Soc., Dalton Trans. (1997) 2645.
[42] P.J. Cornelissen, J.H. Van Diemen, L.R. Groeneveld, J.G. Haasnoot, A.L. Speck, J. Reedjick, Inorg. Chem. 31 (1992) 198.
[43] J. Foley, S. Tyagi, B.J. Hathaway, J. Chem. Soc., Dalton Trans. (1984) 1.
[44] A.W. Addison, T.N. Rao, J. Reedijk, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[45] G. Munno, M. Julve, F. Lloret, J. Faus, M. Verdaguer, A. Caneschi, Angew. Chem., Int. Ed. Engl. 32 (1993) 1046.
[46] P.J. Van Koningsbruggen, D. Gatteschi, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk, C. Zanchini, Inorg. Chem. 34 (1995) 5175.
[47] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. (1989) S1.