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Synthesis and characterization of copper(I)-pyrazole complexes. X-Ray crystal structure of $[Cu(pzH)_2Cl]_2$ and NMR investigation of the fluxional behaviour of $[Cu(pzH)_2(CO)Cl]$

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Abstract

The product of the reduction of $[Cu(pzH)_4Cl_2]$ (pzH = pyrazole, $C_3H_4N_2$) with Cu powder has been shown by single crystal X-ray analysis to be the dimeric species $[Cu(pzH)_2Cl]_2$. The crystals are monoclinic, space group $P2_1/n$, with a 6.327(1), b 9.610(1), c 15.066(1) Å, β 96.91(1), and $Z = 2$. The refinements performed by full-matrix least-squares methods, for 1417 independent significant reflexions, gave a final R value of 0.030. Each dimeric unit, located on a crystallographic inversion centre, contains two Cu atoms (Cu...Cu′ 3.401(1) Å), each surrounded by two bridging Cl atoms and two pzH ligands, in a pseudo-tetrahedral arrangement. The reaction of carbon monoxide with $[Cu(pzH)_2Cl]_2$ gave the new species $[Cu(pzH)_2(CO)Cl]$, which was characterized by IR and NMR spectroscopy. Fluxional behaviour of the pyrazole ligands, equalizing their 3 and 5 positions, was revealed by both ^1H and ^{13}C NMR spectra. Variable temperature ^{13}C NMR experiments in different conditions (solvent or concentrations) led to different E_a values, indicating that the exchange process is not intramolecular, and is favoured in donor solvents, at temperatures above 250 K. In concentrated solutions in CD_2Cl_2 a double-slope Arrhenius plot was obtained, suggesting the occurrence of two different processes, whose natures are discussed.

Introduction

Copper complexes containing pyrazoles (pzH) or pyrazole-derived molecules as ligands are known [1], the most common stoichiometry being $[Cu(pzH)_2X]$ or $[Cu(pzH)_nX_2]$, (X = Cl, Br, NO_3, BF_4; n = 1, 2 or 4), for Cu^I and Cu^{II} respectively.

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The copper(I) complexes [CuL_2BF_4] (L = substituted pyrazoles) were shown by X-ray analysis to contain a two-coordinate Cu^+ cation [2]. In contrast, the supposed ionic nature of [$Cu(pzH)_2Cl$], prepared by Reedijk and co-workers several years ago [3], was based only on the lack of the ν(Cu–Cl) absorptions in its IR spectrum.

We have now prepared Reedijk's complex, with the aim of studying its behaviour towards small molecules, such as CO, CO_2 and O_2, and we report here the spectroscopic characterization of the product of the reaction with carbon monoxide, together with a X-ray investigation of the starting Cu^I complex, which has been shown to be a dimeric species containing bridging chlorine atoms.

Results and discussion

The reduction of [$Cu(pzH)_4Cl_2$] (pzH = pyrazole, $C_3H_4N_2$) with an excess of Cu powder in an alcoholic medium with rigorous exclusion of oxygen, afforded a colourless solution, from which the white "$Cu(pzH)_2Cl$" (compound **1**) was isolated by cooling in an acetone/dry ice bath. The procedure was that reported in ref. 3 except that we did not find it necessary to use an excess of free ligand. Analytical data supported the stoichiometry of the product. However, conductivity measurements, carried out with ethanolic solutions, gave extremely low values, indicating a covalent nature of **1**, in contrast to the conclusion reached in ref. 3. Covalently binding of the Cl atoms was also indicated for the starting copper(II) complex by a neutron diffraction study [4]. We therefore carried out a single crystal X-ray investigation of **1**, which showed that in the solid state the compound has a dimeric structure as illustrated in Fig. 1.

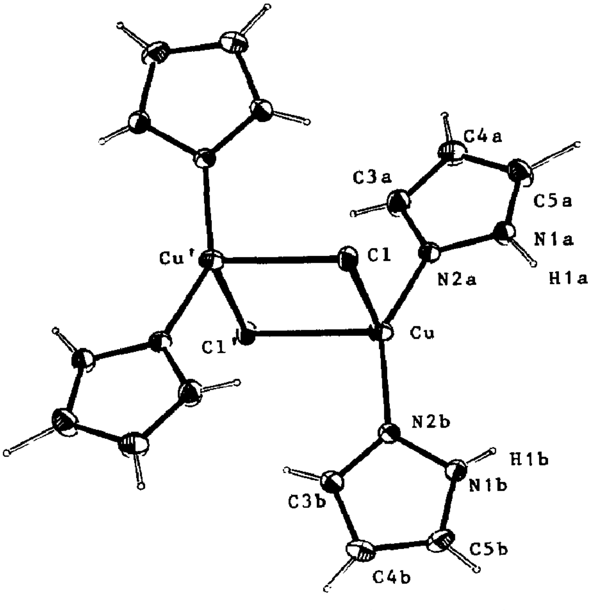


Fig. 1. A view of the dimeric molecule [$Cu(pzH)_2]_2$ (compound **1**) located on a crystallographic inversion center.

Description of the structure of compound 1

The crystals of **1** consist of a molecular packing of discrete dimeric units, located on crystallographic inversion centers. Selected bond distances and angles are listed in Table 1.

The $[Cu(pzH)_2Cl]_2$ dimeric unit contains two Cu^{I} metal centers (Cu...Cu′ 3.401(1) Å), each surrounded by two bridging chlorine atoms and two pyrazole ligands, in a pseudo-tetrahedral arrangement. The highest deviations from ideality are observed for the N2a–Cu–N2b (146.8(9)°) and Cl–Cu–Cl′ (99.3(2)°) angles. The Cu–Cl and Cu–Cl′ bond distances are significantly different, the observed values being 2.526(1) and 2.716(1) Å, respectively. The tetrahedral arrangement around each Cu atom forces the two pzH ligands into a non-coplanar arrangement (dihedral angle between the planes of the two rings 18.1°), whereas in the related complexes $[Cu(pzMe)_2]BF_4$ (pzMe = 1-methylpyrazole) and $[Cu(TMP)_2]BF_4$ (TMP = 1,3,5-trimethylpyrazole) the two substituted pyrazoles are roughly in the same plane (dihedral angles 4.7 and 8.7°, respectively), and show a linear coordination geometry around the Cu^{I} atom (N–Cu–N 178.2(2)° and 173.8(2)°, respectively) [2].

The observed twisting in compound **1** also permits the formation of intermolecular hydrogen bonds, with the $(1 - x, y, z)$ symmetry related moiety, characterized by the following parameters: Cl...H1a 2.42 Å, Cl...N1a 3.22 Å, Cl–H1a–N1a 172.7°, Cl...H1b 2.52 Å, Cl...Nb 3.22 Å, Cl–H1b–N1b 169.8°.

The bond distances and angles within the pyrazole ligands agree well with those previously found for $[Cu(pzMe)_2]BF_4$ (pzMe = 1-methylpyrazole) and $[Cu(TMP)_2]BF_4$ (TMP = 1,3,5-trimethylpyrazole) [2].

Reaction with carbon monoxide

The action of CO on a dichloromethane solution of **1** gives within a few minutes a new species (compound **2**) exhibiting a ν(CO) band in its IR spectrum at 2080 cm^{-1}. This value is in accord with the presence of a coordinated chloride: in fact the

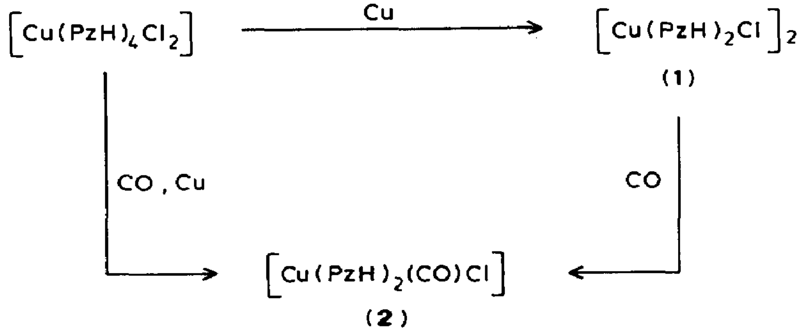
Table 1

Selected bond distances (Å) and angles (°) for compound 1

Cu–Cl	2.526(1)	Cl–Cu–Cl′	99.3(2)
Cu–Cl′	2.716(1)	Cl–Cu–N2a	100.8(6)
Cu–N2a	1.943(2)	Cl–Cu–N2b	100.9(7)
Cu–N2b	1.935(2)	Cl′–Cu–N2a	100.8(6)
		Cl′–Cu–N2b	100.1(6)
		N2a–Cu–N2b	146.8(9)
N1a–N2a	1.343(3)	N2a–N1a–C5a	112.1(2)
N2a–C3a	1.309(4)	N1a–N2a–C3a	104.3(2)
C3a–C4a	1.363(5)	N2a–C3a–C4a	111.8(3)
C4a–C5a	1.357(5)	C3a–C4a–C5a	105.3(3)
C5a–N1a	1.320(4)	N1a–C5a–C4a	106.6(3)
N1b–N2b	1.349(3)	N2b–N1b–C5b	111.8(3)
N2b–C3b	1.328(4)	N1b–N2b–C3b	104.0(2)
C3b–C4b	1.382(4)	N2b–C3b–C4b	111.8(3)
C4b–C5b	1.356(5)	C3b–C4b–C5b	104.4(3)
C5b–N1b	1.326(4)	N1b–C5b–C4b	107.9(2)

carbonylation of the cationic $[Cu(pzH)_2]^+$ complex was reported [2] to give a species with the ν(CO) band at higher frequency (2117 cm^{-1} in CH_2Cl_2), while four-coordinated Cu carbonyl complexes containing N-donor ligands [5] showed a ν(CO) band only at 2080 cm^{-1}. Moreover, the addition of an excess of pyrazole to the solution of compound **2** did not cause any change in position of the ν(CO) band, in contrast to the behaviour reported for $[Cu(pzH)_2(CO)]^+$ [2], which showed a low frequency shift of about 30 cm^{-1} owing to formation of the four-coordinated carbonyl adduct $[Cu(pzH)_3(CO)]^+$.

Compound **2** can be more conveniently prepared by reduction of $[Cu(pzH)_4Cl_2]$ with Cu in the presence of CO bubbling through the solution (see Scheme 1). The nature of the solvent is unimportant: dichloromethane, chloroform, ethanol, methanol, tetrahydrofuran, acetonitrile and acetone can all be used.



Scheme 1

Any attempts to isolate **2** as solid, even by slowly removing the solvent with continuing bubbling of CO failed, and gave a residue containing no CO ligands, and with an IR spectrum identical to that of **1**.

The formulation of **2** as $[Cu(pzH)_2(CO)Cl]$ was supported by the ^{13}C NMR spectrum: in CD_2Cl_2, at room temperature, three signals, at 172.5, 135.0, and 106.0 ppm, respectively, were observed, and their integration ratio was found to be 0.9/4/2 when the spectrum was recorded with ^1H decoupling without NOE. The lower field resonance is due to the carbonyl: this chemical shift agrees well with the values previously reported for copper(I) carbonyl complexes [6]. The other signals have δ values typical for the carbon atoms of the pyrazole ring [7], with the signal of intensity 4 being attributable to carbons C(3) and C(5) adjacent to the N atoms. The ^{13}C NMR spectrum therefore confirms the presence in compound **2** of one carbon monoxide and two equivalent pyrazole ligands.

The ^1H NMR spectrum shows three signals, at δ 12.5 (s, NH), 7.8 (d, J(H–H) 2 Hz, C(3)H + C(5)H) and 6.4 (t, C(4)H), in the integration ratio 1/2/1. Also in this case, only one signal is observed for the positions 3 and 5. Both of the NMR spectra thus indicate the occurrence of some fluxional process equalizing these sites.

The fluxional behaviour of compound 2

As is well known, positions 3 and 5 are usually isochronous in the free pyrazole owing to the tautomerism of the *N*-bound proton. Only in strongly polar solvents [8] or at temperatures below −100 °C [9] is the exchange slow enough to allow observation of the separate ^{13}C resonances for these positions that are also observed in the solid state [10]. Another type of low energy process simulating a mirror which equalizes the sites 3 and 5 is found in some complexes containing anionic η^1-pyrazolyl ligands, and is due to a metal 1,2 shift comparable with that found for the cyclopentadienyl ligand [11]. In complexes containing neutral pyrazoles however, the interchange of the nitrogen sites requires both proton transfer and metal exchange, and so is expected to be more difficult. In line with this, the dynamic behaviour observed for [Ir(3,5Me$_2$pz)(PPh$_3$)$_2$(CO)] disappeared upon protonation to the corresponding pzH cation [12]. The NMR characterization of various pyrazole complexes revealed both static [13] and dynamic [14] behaviour.

When the {^{1}H}-^{13}C NMR spectra are examined at lower temperatures, the resonance due to C(3) and C(5) first broadens, then collapses eventually giving rise

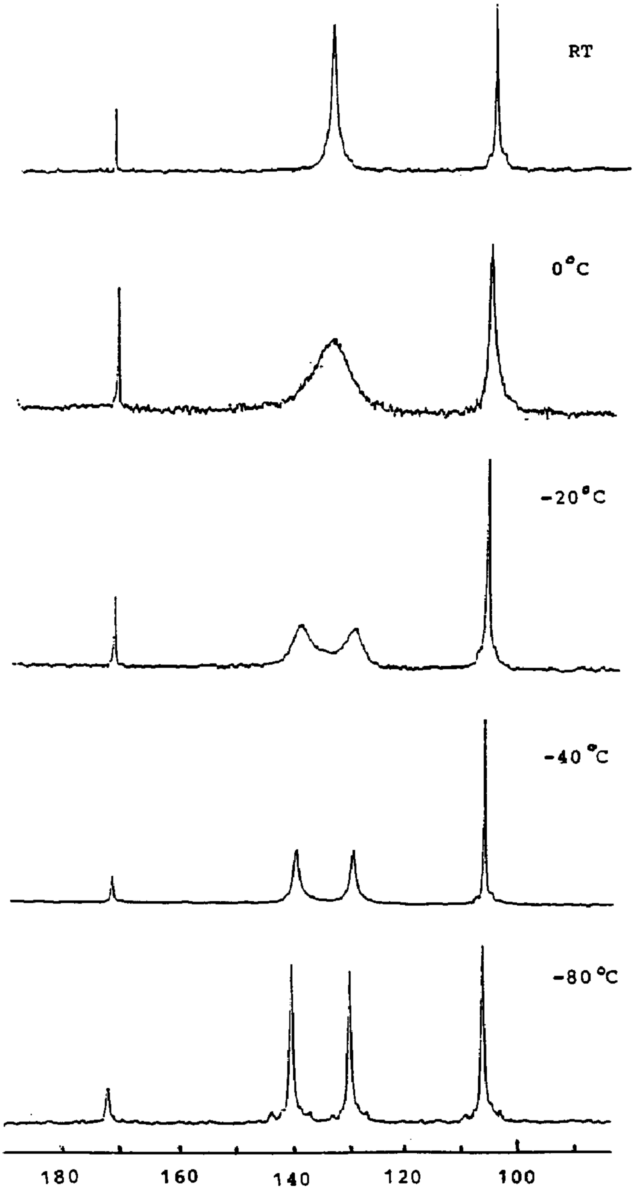


Fig. 2. Variable temperature ^{13}C NMR spectra of [Cu(pzH)$_2$(CO)Cl] (compound **2**) in CD$_2$Cl$_2$.

two well separate signals (140.9 and 130.9 ppm at −80 °C) as the slow exchange region is reached (Fig. 2). A similar behaviour is observed in the ^1H NMR spectrum although H(3) and H(5) have quite close chemical shifts ($\Delta\delta$ 0.05 ppm at 183 K). When the solvent is changed from CD_2Cl_2 to deuterated acetone, the separation of the two signals is more marked ($\Delta\delta$ 0.2 ppm at 183 K). Selective irradiation of the N–H signal at low temperature allowed observation of the fine structure of the other signals: those at δ 8.0 and 7.8 ppm appeared as doublets (J 2.3 and 1.7 Hz, respectively) and that at δ 6.5 ppm, due to C(4)–H, as a pseudo-triplet.

The kinetic constants for the fluxional process at different temperatures were calculated from ^{13}C NMR spectra through the usual approximations for the treatment of two equally populated non-coupled sites [15]. Experiments were performed in order to check the influence of the solvent, of the concentration and of the presence of water. The Arrhenius plots based on the results are shown in Fig. 3 (in CD_2Cl_2 at different concentrations and water contents) and Fig. 4 (in deuterated acetonitrile and acetone). Figure 3 shows that the kinetic constants evaluated for concentrated solutions in methylene chloride, both in presence or in absence of water, followed different trends at high and low temperatures, indicating the presence of two possible mechanisms with different activation energies (6.2 ± 0.2 kcal/mol at low temperature and 11.6 ± 0.1 kcal/mol at higher temperature). This is not the case with more dilute solutions in the same solvent, for which the

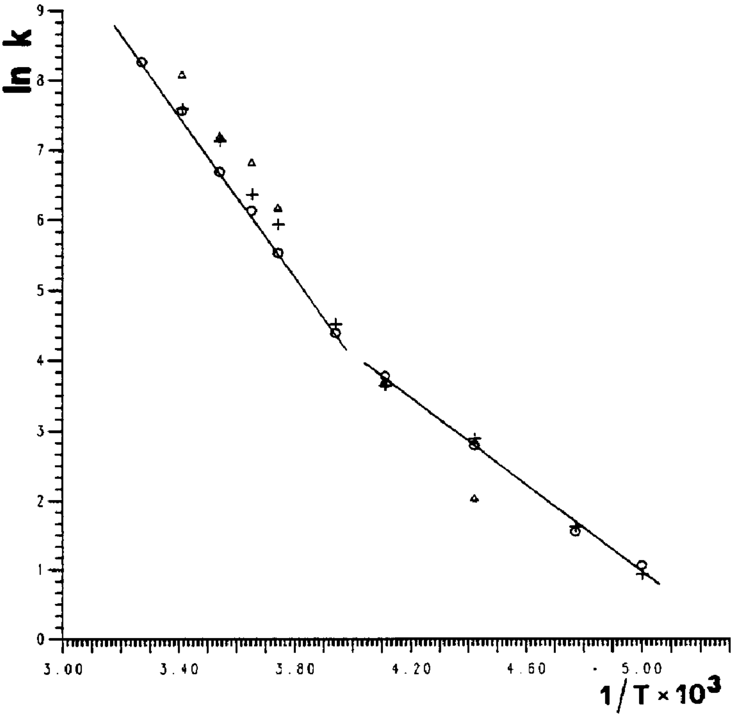


Fig. 3. Arrhenius plot for the kinetic constants obtained in CD_2Cl_2 solution: ○ concentrated (1 *M*) and anhydrous solution; + concentrated (1 *M*) solution saturated with water; △ dilute (0.2 *M*) and anhydrous solution. For the experiment in concentrated anhydrous solution (○) the least-square fits are also shown. At temperatures below 220 K no measurable broadening could be observed in the dilute solution (△).

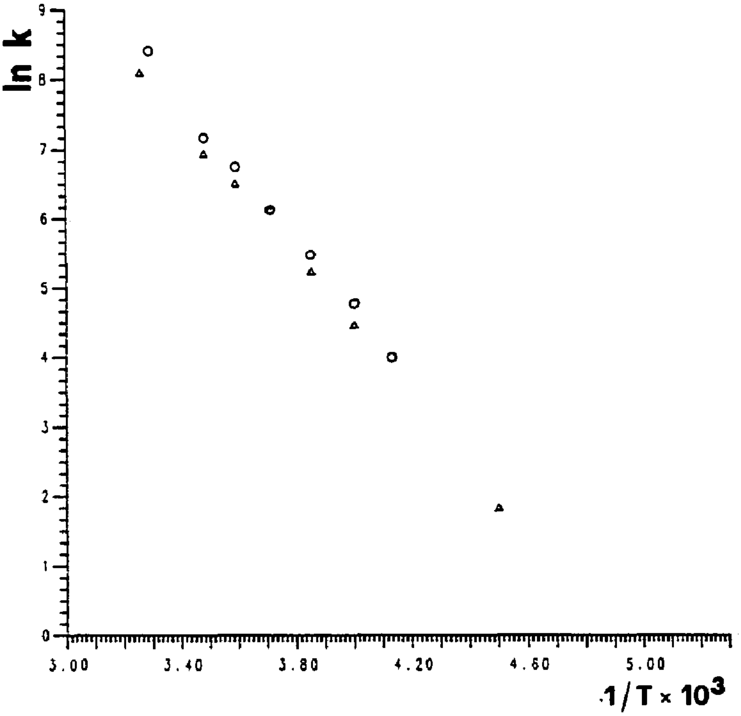


Fig. 4. Arrhenius plot for the kinetic constants obtained for deuterated acetone (△) and acetonitrile (○) solutions (1 *M*).

experimental data indicate a single activation energy (12.1 ± 0.2 kcal/mol). There is also simple behaviour in acetone or acetonitrile with only one activation energy in the range of examined temperatures ($E_a = 10.0 \pm 0.2$ and 10.1 ± 0.2 kcal/mol, respectively).

The variation of the activation energy on changing the solvent or the concentration suggests that the exchange does not occur by an intramolecular process. The process seems also not to involve a deprotonation of the pyrazoles by water acting as a base, since no significant differences in the rate constants were observed for anhydrous or wet solvents. The behaviour observed at low temperatures in methylene chloride is probably due to a cooperative mechanism which involves solute–solute interactions. An associative process for the N–H tautomerism was also observed for concentrated solutions of the free pyrazole itself [9], with E_a of 4.8 kcal/mole (at $T > 203$ K). The mechanism with the higher activation energy, which operated at temperatures above 250 K, and over the whole range of temperature in the case of dilute solutions, could be of dissociative type, i.e. involving the tautomerization in the free pyrazole. This could also be the mechanism operating in acetone or acetonitrile: the stabilization of the intermediate by the coordination of a solvent molecule could account for the lower activation energy.

Experimental

All reactions were performed under Ar or CO, in solvents deoxygenated and dried by standard methods. The IR spectra were recorded on a Perkin–Elmer 781 grating spectrophotometer and the NMR spectra on a Bruker WP 80 spectrometer. [$Cu(pzH)_4Cl_2$] was prepared as previously described [16]. [$Cu(pzH)_2Cl]_2$ was obtained by the method reported in ref. 3 but without use of an excess of free pyrazole. The sample used for the X-ray crystal structure determination was obtained by slow diffusion of n-hexane into a dichloromethane solution..

Synthesis of [$Cu(pzH)_2COCl$]

(a) Carbon monoxide was bubbled through CH_2Cl_2 (5 ml), then [$Cu(pzH)_2Cl]_2$ (0.19 mmol) was added. After 10 min, with continuous bubbling of CO, the IR of the colourless solution showed the presence of a strong ν(CO) absorption at 2080 cm^{-1}. Attempts made to isolate the carbonyl complex failed, the starting material, [$Cu(pzH)_2Cl]_2$, being recovered in all cases.

(b) Carbon monoxide was bubbled through CH_2Cl_2 (5 ml), then [$Cu(pzH)_4Cl]_2$ (0.25 mmol) and Cu powder were added with stirring. After 30 min with continuous bubbling of CO the initially blue suspension was converted into a colourless solution. The excess of Cu powder was removed by filtration under CO, and the IR spectrum showed the strong band at 2080 cm^{-1}, which remained unchanged when free ligand was added.

The samples used for the ^{13}C NMR experiments were prepared in this way in deuterated solvents, and the solutions were filtered directly into the NMR tubes, which were then sealed under CO. In the variable temperature experiments, the

Table 2

Crystal data and intensity collection parameters for compound **1**

Compound	[$Cu(pzH)_2Cl]_2$
Formula	$C_{12}H_{16}Cl_2Cu_2N_8$
Formula weight (uma)	470.30
Crystal system	monoclinic
a (Å)	6.327(1)
b (Å)	9.610(1)
c (Å)	15.066(1)
β (°)	96.91(1)
U (Å)	909.4(2)
Z, D_{calc} (g cm^{-3})	2, 1.71
Space group	$P2_1/n$ (no. 14)
μ (Mo-K_α), cm^{-1}	26.54
Scan mode	ω
ω-scan width (°)	$1.4 + 0.35 \tan \theta$
θ-range (°)	3–25
Collected octants	$+h$, $+k$, $\pm l$
Measured reflections	1741
Unique observed reflections with $I > 3\sigma(I)$	1406
Min transmission factor	0.80
Crystal dimensions, mm	$0.20 \times 0.20 \times 0.25$
Final R and R_w indices	0.030, 0.054
ESD	1.418
No. of variable parameters	142

$R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]$

ESD = $[\Sigma w(F_o - k|F_c|)^2/(NO - NV)]$

Table 3

Fractional atomic coordinates for compound **1**

Atom	x	y	z
Cu	0.68620(6)	0.42106(4)	0.44495(2)
Cl	0.2872(1)	0.38837(8)	0.42107(5)
N1A	0.9770(4)	0.2152(3)	0.5347(2)
N2A	0.7737(4)	0.2533(2)	0.5114(1)
C3A	0.6630(5)	0.1621(4)	0.5510(2)
C4A	0.7907(7)	0.0670(4)	0.5982(3)
C5A	0.9925(6)	0.1045(4)	0.5870(3)
N1B	0.9103(4)	0.5643(2)	0.3101(2)
N2B	0.7272(4)	0.5407(2)	0.3451(1)
C3B	0.5847(5)	0.6181(3)	0.2955(2)
C4B	0.6744(6)	0.6888(4)	0.2294(2)
C5B	0.8825(5)	0.6516(4)	0.2415(2)
H1A	1.063(7)	0.254(4)	0.509(2)
H3A	0.525(7)	0.155(4)	0.531(3)
H4A	0.751(6)	−0.003(4)	0.631(2)
H5A	1.147(7)	0.063(4)	0.621(2)
H1B	1.004(4)	0.527(3)	0.330(2)
H3B	0.464(5)	0.624(4)	0.307(2)
H4B	0.600(6)	0.761(3)	0.196(2)
H5B	0.987(5)	0.683(3)	0.216(2)

temperatures were controlled by the B-VT 1000 equipment of the instrument, and calibrated immediately before the acquisition of the spectra with an acetone/CCl_4 solution [17].

Crystal structure determination. The crystal data and the data-collection/analysis parameters used in the determination of the structure of compound **1** are summarized in Table 2. The diffraction experiments were performed on an Enraf–Nonius CAD4 diffractometer at room temperature, using graphite monochromatized Mo-K_α radiation (λ 0.71073 Å). The unit cell parameters were determined by least squares fitting of the setting angles of 25 high intensity reflections, with $20° < 2\theta < 28°$. The diffraction intensities were corrected for Lorentz, polarization, and absorption (empirical correction) [18]. Anomalous dispersion corrections for atomic scattering factors were taken from ref. 19.

The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares, the minimized function being $\Sigma w(F_o - k\,|\,F_c\,|)^2$. Weights assigned to individual observations were $w = 1/\sigma(F_o)^2$, where $\sigma(F_o) = [\sigma^2(I) + (0.07I)^2]^{1/2}/2F_o\mathrm{Lp}$.

All the non-hydrogen atoms were given anisotropic temperature factors, while hydrogen atoms were refined with isotropic B's. The primary extinction coefficient was also refined, to a value of $1.8(1) \times 10^{-6}$.

The choice of the identities (C or N) of the atoms adjacent to the coordinated nitrogen atoms was based on: (i) the uniformity of thermal vibrations amplitudes; (ii) the observed bond distances and angles in the pyrazole ligands; and (iii) the presence of hydrogen bonds through the "acidic" N–H groups.

All the computations were carried out on a PDP 11/73 computer using the Enraf–Nonius SDP package of crystallographic programs [20] and the physical constants tabulated therein. The atomic coordinates are listed in Table 3. List of anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

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