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Note

Synthesis, properties and molecular structure of copper(II) and cobalt(II) 1,2-bis(pyrazol-1-ylmethyl)benzene complexes

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Abstract

The synthesis of a new bifunctional ligand, 1,2-bis(pyrazol-1-ylmethyl)benzene (L), and the structures of its complexes with Cu(II) and Co(II) ions are described. Ligand L reacts with copper(II) chloride to form two isomers: the green isomer is $[CuLCl_2]\cdot 0.5CH_3OH$ (**1**), and the yellowish-green isomer is $[Cu_2L_2Cl_4]$ (**2**). The ligand reacts with cobalt(II) chloride to form a blue complex, $[CoLCl_2]$ (**3**). The molecular structures of complexes **1**, **2** and **3** have been characterized by X-ray diffraction: **1** monoclinic, space group $P2_1/n$, $Z=8$, $a=15.465(5)$, $b=13.378(6)$, $c=16.309(6)$ Å, $\beta=100.98(3)°$; **2** triclinic, space group $P\bar{1}$, $Z=1$, $a=8.252(4)$, $b=9.147(8)$, $c=10.414(6)$ Å, $\alpha=107.05(6)$, $\beta=101.37(4)$, $\gamma=89.26(6)°$; **3** monoclinic, space group $P2_1/c$, $Z=4$, $a=10.364(1)$, $b=11.617(3)$, $c=13.720(2)$ Å, $\beta=109.76(1)°$. The coordination sphere of the metal(II) ion in complexes **1** and **3** has a distorted tetrahedral geometry, while that in complex **2** has a distorted square-pyramidal geometry.

Keywords: Crystal structures; Copper complexes; Cobalt complexes; Polyfunctional ligand complexes

1. Introduction

Polyfunctional ligands derived from pyrazole, imidazole, triazole and pyridazine [1–4] can form transition-metal complexes in which the metals are brought into close proximity. Molecular structure characterizations of these complexes have been pursued vigorously in many laboratories, because these complexes are used as potential models for biological dimetallic sites [5]. Some dicopper(II) complexes with pyrazolyl ligands have been studied as potential models for hemocyanin by Sorrel and co-workers [6]. Reedijk and co-workers reported that pyrazolyl ligands offered N-donor sites to form halido-bridged copper(II) complexes [1,7]. In this paper, we report the investigation of the complexing properties of the pyrazolyl ligand 1,2-bis(pyrazol-1-ylmethyl)benzene (L), which is a bidentate ligand with two N-donor sites on the pyrazolyl rings. The crystal structures of its copper(II) and cobalt(II) complexes, including the monomeric complexes $[CuLCl_2]\cdot 0.5CH_3OH$ and $[CoLCl_2]$ and the dimeric complex $[Cu_2L_2Cl_4]$, have been determined. The spectroscopic and electrochemical properties of these complexes are also reported.

2. Experimental

2.1. Syntheses

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. 1,2-Bis(bromomethyl)benzene was prepared according to the literature method [8].

2.1.1. 1,2-Bis(pyrazol-1-ylmethyl)benzene (L)
Pyrazole (1.36 g, 20 mmol) and sodium carbonate (2.12 g, 20 mmol) were added to benzene (20 ml), and then 1,2-bis(bromomethyl)benzene (2.64 g, 10 mmol) in benzene (20 ml) was added to the solution. After refluxing for 6 h, the solvents were removed under reduced pressure by rotary evaporation. The residue was washed with acetone and filtered. The product was purified by column chromatography (silica gel 60) using

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ethyl acetate–hexane (1:4) ($R_f = 0.51$), giving a pale yellow oil. Yield 1.30 g (55%). *Anal.* Found: C, 70.21; H, 5.96; N, 23.32. Calc. for $C_{14}H_{14}N_4$: C, 70.57; H, 5.92; N, 23.51%. MS: *m/z* 238, 170. ^{1}H NMR ($CDCl_3$): $\delta = 5.30$ (4H, s, aryl CH_2N), 6.23 (2H, m, pyrazolyl C^4–H), 7.05 (2H, m, pyrazole C^5–H), 7.26 (4H, m, aryl H), 7.52 (2H, m, pyrazolyl C^3–H).

2.1.2. $[CuLCl_2] \cdot 0.5CH_3OH$ (1) and $[Cu_2L_2Cl_4]$ (2)

Copper(II) chloride dihydrate (170 mg, 1 mmol) and L (238 mg, 1 mmol) were dissolved in methanol (40 ml), and then the mixture was filtered to remove impurities. Green and yellowish-green crystals were obtained by slow diffusion of diethyl ether into the methanol solution. The green crystals are complex **1**. *Anal.* Found: C, 44.78; H, 3.98; N, 14.20. Calc. for $C_{14.5}H_{16}Cl_2CuN_4O_{0.5}$: C, 44.80; H, 4.14; N, 14.41%. The yellowish-green crystals are complex **2**. *Anal.* Found: C, 45.14; H, 3.83; N, 14.77. Calc. for $C_{28}H_{28}Cl_4Cu_2N_8$: C, 45.11; H, 3.98; N, 15.03%.

2.1.3. $[CoLCl_2]$ (3)

Cobalt(II) chloride hexahydrate (238 mg, 1 mmol) and L (238 mg, 1 mmol) were dissolved in methanol (40 ml), and then the mixture was filtered to remove impurities. Blue crystals were obtained by slow diffusion of diethyl ether into the methanol solution. *Anal.* Found: C, 45.81; H, 3.86; N, 15.03. Calc. for $C_{14}H_{14}Cl_2CoN_4$: C, 45.68; H, 3.83; N, 15.22%.

2.2. Physical measurements

^{1}H NMR spectra were recorded on a Bruker AM-200WB instrument at 200 MHz using $CDCl_3$ as the solvent, and ESR spectra were recorded on a Bruker ESP 300 X-band instrument using diphenylpicrylhydrazyl (dpph) as a standard. Magnetic susceptibilities were measured using the Faraday method on a CAHN 2000 instrument with $Hg[Co(SCN)_4]$ as a standard, and diamagnetic corrections were made using Pascal's constants. Mass spectra were recorded on a Finnigan MAT TSQ-46C instrument, and IR spectra on a BIO-RAD FTS-40 spectrometer using KBr as the support. Elemental analyses were obtained using a Perkin-Elmer 2400 analyzer instrument. Electrochemistry was performed with a Bioanalytical System model CV-27 potentiostat and a BAS X–Y recorder. Cyclic voltammetry (CV) was conducted using a three-electrode cell: a BAS glassy carbon working electrode (with an area of 0.07 cm^2), a platinum-wire auxiliary electrode and an Ag/AgCl(saturated KCl) reference electrode; TBAP ((tetra-n-butyl)ammonium perchlorate) was the supporting electrolyte and CH_3CN was the solvent. The absorption spectra were obtained with a Hewlett-Packard 8452A diode-array spectrophotometer.

2.3. Structure determination

For the structure determination, suitable crystals of the complexes were chosen. Intensity data were collected at 25 °C on a CAD-4 diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The unit-cell constants were derived from a least-squares refinement of 25 setting reflections. The θ–2θ scan technique and a variable scan speed were used to obtain the integrated intensities. Three reference reflections were monitored throughout the measurements; the

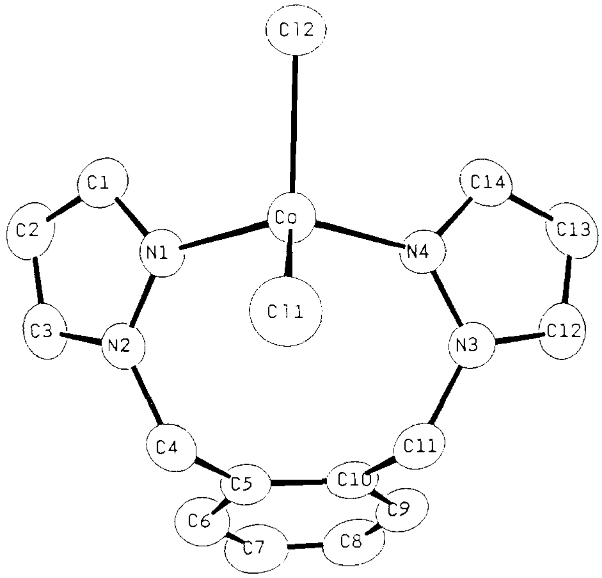

Fig. 1. The crystal structure of molecule A of complex **1**.

Table 1
Crystallographic data for complexes **1** and **2**

Complex	**1**	**2**
Formula	$[CuLCl_2] \cdot 0.5CH_3OH$	$[Cu_2L_2Cl_4]$
Molecular weight	388.76	745.49
Crystal size (mm)	0.40×0.50×0.50	0.13×0.25×0.63
Crystal	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	15.465(5)	8.252(4)
b (Å)	13.378(6)	9.147(8)
c (Å)	16.309(6)	10.414(6)
α (°)		107.05(6)
β (°)	100.98(3)	101.37(4)
γ (°)		89.26(6)
V (Å^3)	3312.4(22)	735.9(8)
Z	8	1
$F(000)$	1584	378
D_c (Mg m^{-3})	1.559	1.682
μ (mm^{-1})	1.65	1.85
2θ Range (°)	2–50	2–50
Ranges of h, k, l	−16–16, 0–14, 0–17	−9–9, 0–10, −12–11
Scan parameters	$1.3 + 0.7\tan\theta$	$2.0 + 0.7\tan\theta$
Total no. reflections	4309 ($3228 > 2\sigma$)	2587 ($2182 > 2\sigma$)
R, R'[a]	0.038, 0.031	0.051, 0.068
S[b]	2.80	2.24

[a] $R = \Sigma(F_o - F_c)/\Sigma(F_o)$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$.

[b] $S = [\Sigma w(F_o - F_c)^2/(\text{no. of reflns.} - \text{no. of params.})]^{1/2}$.

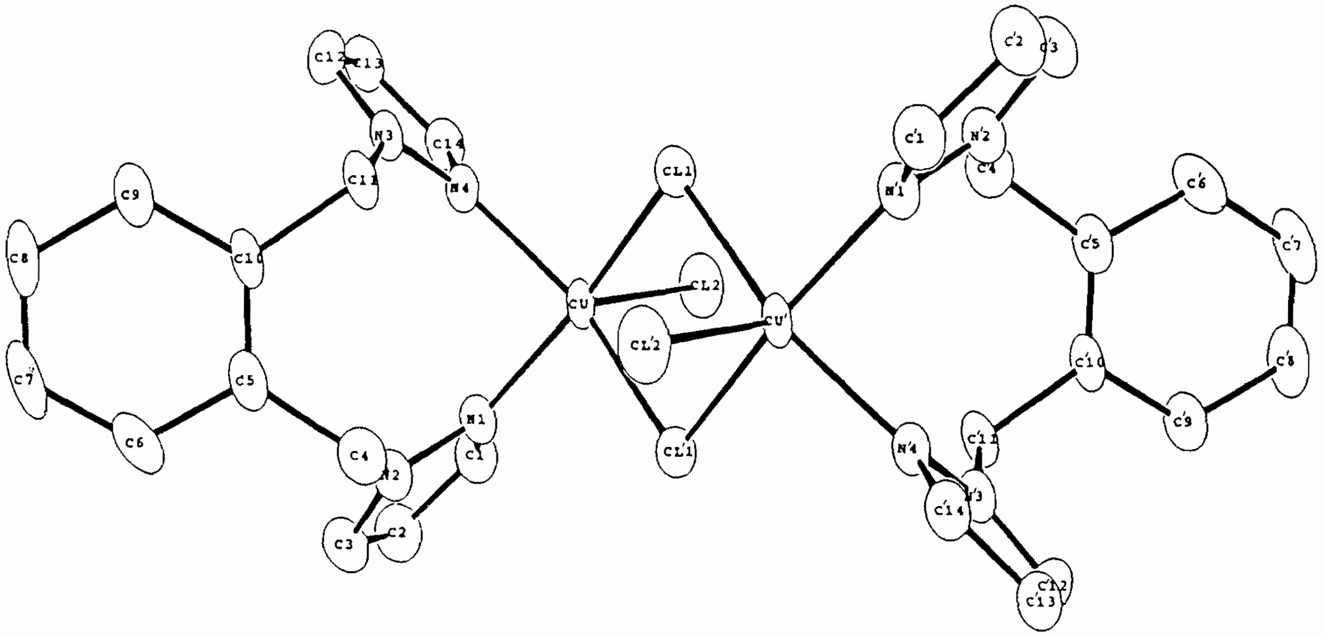

Fig. 2. The molecular structure of complex **2**.

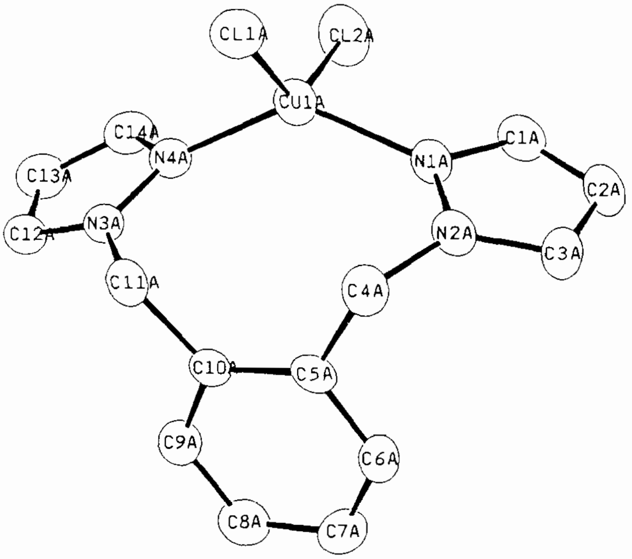

Fig. 3. The molecular structure of complex **3**.

Table 2
Crystallographic data for complex **3**

Formula	[CoLCl$_2$]
Molecular weight	368.13
Crystal size (mm)	0.40×0.50×0.50
Crystal	monoclinic
Space group	$P2_1/c$
a (Å)	10.364(1)
b (Å)	11.617(3)
c (Å)	13.720(2)
β (°)	109.76(1)
V (Å^3)	1554.6(5)
Z	4
F(000)	748
D_c (Mg m^{-3})	1.573
μ (mm^{-1})	1.45
2θ Range (°)	2–50
Ranges of h, k, l	−12–11, 0–13, 0–16
Scan parameters	1.3+0.7tan θ
Total no. reflections	2740 (2208>2σ)
R, R'[a]	0.028, 0.022
S[a]	2.26

[a] Same as in Table 1.

variation of the intensities was less than 2% for complexes **1** and **3**, and less than 6% for complex **2**. Absorption corrections were applied according to the experimental Ψ rotation curve. The molecular structures of complexes **1**–**3** are shown in Figs. 1–3. Crystal data are given in Tables 1 and 2. Selected bond distances and angles are shown in Tables 3 and 4.

The structures were solved by the heavy-atom method. The atomic parameters were obtained from the subsequent Fourier syntheses and the least-squares refinements. The final results for the non-hydrogen atoms of complexes **1**, **2** and **3** are given in Tables 5, 6 and 7, respectively. The weighting scheme of the form $1/[\sigma^2(F_o)]$ was used. All the hydrogen-atom parameters were calculated according to the ideal geometry and were not refined. The structural analyses were carried out on a Microvax III computer using NRCVAX programs [9]. Atomic scattering factors were taken from the literature [10].

Table 3
Selected bond distances (Å) and angles (°) of complexes **1** and **2**

Complex **1**			
Cu(1A)–N(1A)	1.984(4)	Cu(1A)–Cl(1A)	2.216(2)
Cu(1A)–N(4A)	1.984(4)	Cu(1A)–Cl(2A)	2.225(2)
Cu(1B)–N(1B)	1.963(4)	Cu(1B)–Cl(1B)	2.234(2)
Cu(1B)–N(4B)	1.961(4)	Cu(1B)–Cl(2B)	2.244(2)
Cl(1A)–Cu(1A)–Cl(2A)	132.87(7)	Cl(1A)–Cu(1A)–N(1A)	100.68(12)
Cl(1A)–Cu(1A)–N(4A)	100.41(13)	Cl(2A)–Cu(1A)–N(1A)	97.50(13)
Cl(2A)–Cu(1A)–N(4A)	97.08(13)	N(1A)–Cu(1A)–N(4A)	134.24(16)
Cl(1B)–Cu(1B)–Cl(2B)	133.92(8)	Cl(1B)–Cu(1B)–N(1B)	97.25(14)
Cl(1B)–Cu(1B)–N(4B)	95.08(13)	Cl(2B)–Cu(1B)–N(1B)	96.93(13)
Cl(2B)–Cu(1B)–N(4B)	95.01(13)	N(1B)–Cu(1B)–N(4B)	148.62(18)
Complex **2**			
Cu···Cu′	3.480(3)	Cu–Cl(1)	2.372(2)
Cu–Cl′(1)	2.341(3)	Cu–N(1)	1.991(6)
Cu–N(4)	2.001(6)	Cu–Cl(2)	2.374(3)
Cl(1)–Cu–Cl′(1)	84.81(9)	Cu–Cl(1)–Cu′	95.19(9)
Cl(1)–Cu–N(1)	89.3(2)	Cl(1)–Cu–N(4)	155.2(2)
Cl(1)–Cu–Cl(2)	101.95(9)	Cl′(1)–Cu–N(1)	161.8(2)
Cl′(1)–Cu–N(4)	90.3(2)	Cl′(1)–Cu–Cl(2)	97.8(1)
N(1)–Cu–N(4)	87.9(2)	N(1)–Cu–Cl(2)	100.2(2)
N(4)–Cu–Cl(2)	102.8(2)		

Table 4
Selected bond distances (Å) and angles (°) of complex **3**

Co–Cl(1)	2.2399(9)	Co–Cl(2)	2.2395(9)
Co–N(1)	1.997(2)	Co–N(4)	2.011(2)
Cl(1)–Co–Cl(2)	115.50(3)	Cl(1)–Co–N(1)	109.60(7)
Cl(1)–Co–N(4)	112.71(6)	Cl(2)–Co–N(1)	105.46(7)
Cl(2)–Co–N(4)	102.56(6)	N(1)–Co–N(4)	110.62(8)

3. Results and discussion

3.1. Molecular structures of complexes 1–3

Complex **1** is a monocopper(II) complex. There is 0.5 methanol molecule as solvent and it is disordered. Each copper(II) ion is coordinated by two nitrogen atoms (N(1), N(4)) from pyrazolyl rings of the ligand L and two chloride ions (Cl(1), Cl(2)). The two Cu(1A)–N distances are both 1.984(4) Å, and the two Cu(1A)–Cl distances are 2.216(2) and 2.225(2) Å, respectively. However, the Cu(1B)–N distances are 1.963(4) and 1.961(4) Å, which are shorter than the Cu(1A)–N distance. All of the Cu–N(pyrazole) distances are within the range of other Cu–N(pyrazole) distances of four-coordinated Cu(II) complexes [11,12]. The Cu(1B)–Cl distances are 2.234(2) and 2.244(2) Å, which are longer than the Cu(1A)–Cl distances, and the two Cl(1)–Cu–Cl(2) angles are 132.87(7)° and 133.92(8)°, indicating that the coordination spheres of both copper(II) ions have strongly distorted tetrahedral geometries.

Each copper(II) ion of complex **2** is coordinated by five donors: two pyrazolyl nitrogen atoms (N(1), N(4)) at 1.991(6) and 2.001(6) Å, two bridging chloride ions (Cl(1), Cl′(1)) at 2.372(2) and 2.341(3) Å and a non-bridging chloride ion (Cl(2)) at 2.374(3) Å that occupies the fifth coordination site. Two copper(II) ions and two bridging chloride ions form a centrosymmetric planar four-membered ring. The Cu–Cl–Cu′ bridging angle is 95.19(9)°, and the Cl–Cu–Cl′ angle is 84.81(9)°. The Cu···Cu′ distance is 3.480(3) Å. The coordination geometry is not perfectly square-pyramidal. Addison et al. [13] defined the τ parameter ($\tau = 0$, square-pyramidal geometry; $\tau = 1$, trigonal-bipyramidal geometry) to distinguish between a square-pyramidal geometry and a trigonal-bipyramidal geometry. The τ value for complex **2** is 0.110, indicating that the structure can be described as having a distorted square-pyramidal geometry. The basal plane involves N(1), N(4), Cl(1) and Cl′(1), while another Cl(2) occupies the apical position. The Cu(II) ion is 0.403 Å above the basal plane. In the literature there are several well-characterized examples of five-coordinated dicopper(II) compounds. Hodgson and coworkers [14] studied a series of these bis(μ-halido)copper(II) complexes and described the structure of these complexes. The distances and angles in complex **2** are normal, compared with the known compounds.

The structure of complex **3** is similar to that of complex **1**. The two Co–N distances, 1.997(2) and 2.011(2) Å, are similar in value [15,16]. The two Co–Cl distances are 2.2399(9) and 2.2395(9) Å, respectively. The N(1)–Co–N(4), Cl(1)–Co–Cl(2) and Cl(1)–Co–N(1) angles are 110.62(8)°, 115.50(3)° and 109.60(7)°, re-

Table 5
Final atomic positional parameters of non-hydrogen atoms for complex **1**

Atom	x	y	z	B_{eq}[a] (Å^2)
Cu(1A)	0.74167(4)	0.33045(5)	0.28718(4)	2.83(3)
Cl(1A)	0.82173(10)	0.38433(11)	0.19698(8)	3.47(7)
Cl(2A)	0.61423(10)	0.24885(12)	0.27193(11)	4.76(9)
N(1A)	0.8182(3)	0.2220(3)	0.34343(24)	2.51(21)
N(2A)	0.9045(3)	0.2307(3)	0.37841(25)	2.71(21)
N(3A)	0.7500(3)	0.5398(3)	0.35349(24)	2.61(21)
N(4A)	0.6992(3)	0.4595(3)	0.32460(24)	2.61(21)
C(1A)	0.7992(3)	0.1259(4)	0.3478(3)	3.0(3)
C(2A)	0.8722(4)	0.0734(4)	0.3854(3)	3.6(3)
C(3A)	0.9383(3)	0.1422(4)	0.4048(3)	3.4(3)
C(4A)	0.9477(3)	0.3284(4)	0.3921(3)	2.8(3)
C(5A)	0.9220(3)	0.3842(4)	0.4647(3)	2.35(24)
C(6A)	0.9498(3)	0.3418(4)	0.5435(3)	3.1(3)
C(7A)	0.9313(4)	0.3857(4)	0.6143(3)	3.6(3)
C(8A)	0.8840(4)	0.4734(4)	0.6075(3)	3.5(3)
C(9A)	0.8562(4)	0.5169(4)	0.5298(3)	3.4(3)
C(10A)	0.8751(3)	0.4738(4)	0.4579(3)	2.35(24)
C(11A)	0.8455(3)	0.5314(4)	0.3769(3)	2.8(3)
C(12A)	0.7004(4)	0.6191(4)	0.3635(3)	3.6(3)
C(13A)	0.6142(4)	0.5913(4)	0.3395(3)	4.2(3)
C(14A)	0.6169(3)	0.4922(4)	0.3161(3)	3.5(3)
Cu(1B)	0.69942(5)	0.32946(5)	0.87452(4)	3.57(4)
Cl(1B)	0.63329(15)	0.30195(15)	0.74231(11)	8.54(13)
Cl(2B)	0.66348(9)	0.29710(11)	0.99883(9)	3.70(7)
N(1B)	0.7911(3)	0.2268(3)	0.8805(3)	3.62(24)
N(2B)	0.8642(3)	0.2245(3)	0.9411(3)	3.39(23)
N(3B)	0.7107(3)	0.5411(3)	0.92785(24)	2.89(21)
N(4B)	0.6682(3)	0.4716(3)	0.8740(3)	3.00(22)
C(1B)	0.7911(4)	0.1423(4)	0.8386(4)	4.7(3)
C(2B)	0.8643(5)	0.0861(5)	0.8726(4)	6.0(4)
C(3B)	0.9096(4)	0.1408(4)	0.9372(4)	4.9(3)
C(4B)	0.8913(3)	0.3114(4)	0.9923(3)	3.2(3)
C(5B)	0.9101(3)	0.4002(4)	0.9398(3)	2.5(3)
C(6B)	0.9753(3)	0.3870(4)	0.8935(3)	3.5(3)
C(7B)	0.9975(4)	0.4621(4)	0.8436(3)	3.7(3)
C(8B)	0.9546(4)	0.5528(4)	0.8398(3)	3.7(3)
C(9B)	0.8892(4)	0.5662(4)	0.8844(3)	3.3(3)
C(10B)	0.8657(3)	0.4914(4)	0.9357(3)	2.5(3)
C(11B)	0.7934(3)	0.5166(4)	0.9840(3)	2.8(3)
C(12B)	0.6679(4)	0.6288(4)	0.9168(4)	4.2(3)
C(13B)	0.5955(4)	0.6157(4)	0.8556(4)	4.8(3)
C(14B)	0.5979(4)	0.5178(4)	0.8307(3)	3.8(3)
C	0.1677(5)	0.1483(6)	0.0171(5)	8.12(22)
O	0.0917(6)	0.1735(7)	0.0528(5)	6.56(23)
O′	0.1446(8)	0.2245(9)	−0.0135(7)	10.8(4)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table 6
Final atomic positional parameters of non-hydrogen atoms for complex **2**

Atom	x	y	z	B_{eq}[a] (Å^2)
Cu	0.49236(11)	0.08448(9)	0.17157(9)	2.14(3)
Cl(1)	0.65506(23)	0.10904(19)	0.01433(19)	2.84(7)
Cl(2)	0.6534(3)	−0.07496(23)	0.28529(22)	3.76(9)
N(1)	0.5814(7)	0.2899(6)	0.2946(6)	2.49(25)
N(2)	0.5446(8)	0.4276(6)	0.2681(6)	2.7(3)
N(3)	0.1421(7)	0.1564(6)	0.2022(6)	2.35(25)
N(4)	0.2943(7)	0.1163(6)	0.2590(6)	2.23(24)
C(1)	0.6839(10)	0.3263(8)	0.4136(7)	2.9(3)
C(2)	0.7192(10)	0.4829(9)	0.4667(8)	3.6(4)
C(3)	0.6279(10)	0.5423(8)	0.3703(9)	3.5(4)
C(4)	0.4314(10)	0.4361(8)	0.1436(8)	3.0(3)
C(5)	0.2605(9)	0.4906(8)	0.1658(7)	2.6(3)
C(6)	0.2463(11)	0.6512(8)	0.2117(9)	3.6(4)
C(7)	0.0939(12)	0.7098(8)	0.2315(9)	4.2(4)
C(8)	−0.0417(11)	0.6173(9)	0.2057(9)	3.9(4)
C(9)	−0.0316(10)	0.4585(8)	0.1581(8)	3.2(4)
C(10)	0.1221(9)	0.3965(7)	0.1387(7)	2.4(3)
C(11)	0.1192(9)	0.2210(7)	0.0876(7)	2.5(3)
C(12)	0.0365(9)	0.1556(8)	0.2849(9)	3.2(4)
C(13)	0.1183(10)	0.1167(8)	0.3959(8)	3.1(3)
C(14)	0.2780(9)	0.0933(8)	0.3741(7)	2.6(3)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table 7
Final atomic positional parameters of non-hydrogen atoms for complex **3**

Atom	x	y	z	B_{eq}[a] (Å^2)
Co	0.72079(4)	0.14583(3)	0.22677(3)	3.163(18)
Cl(1)	0.78447(8)	0.12716(7)	0.39909(5)	4.59(4)
Cl(2)	0.67100(7)	0.32533(6)	0.16620(6)	4.62(4)
N(1)	0.55060(21)	0.05449(18)	0.15951(16)	3.11(11)
N(2)	0.52395(21)	−0.05766(19)	0.17171(17)	3.25(11)
N(3)	0.95831(21)	0.01072(18)	0.20255(16)	3.16(11)
N(4)	0.86936(20)	0.09955(17)	0.17089(15)	2.78(10)
C(1)	0.4370(3)	0.09522(24)	0.08809(21)	3.52(14)
C(2)	0.3391(3)	0.0102(3)	0.05486(21)	3.82(14)
C(3)	0.3974(3)	−0.08530(25)	0.10919(23)	3.88(14)
C(4)	0.6268(3)	−0.13285(24)	0.24284(20)	3.69(14)
C(5)	0.7062(3)	−0.20223(23)	0.18868(21)	3.43(14)
C(6)	0.6395(3)	−0.2964(3)	0.1305(3)	4.66(17)
C(7)	0.7008(3)	−0.3634(3)	0.07590(25)	5.25(18)
C(8)	0.8323(3)	−0.3373(3)	0.07915(23)	4.94(18)
C(9)	0.9007(3)	−0.2461(3)	0.13778(23)	3.94(15)
C(10)	0.8407(3)	−0.17811(22)	0.19388(20)	3.23(13)
C(11)	0.9299(3)	−0.08494(23)	0.26187(20)	3.45(13)
C(12)	1.0606(3)	0.0207(3)	0.16326(24)	4.18(17)
C(13)	1.0375(3)	0.1170(3)	0.10421(22)	4.03(16)
C(14)	0.9180(3)	0.16354(23)	0.11044(19)	3.27(13)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

spectively. The angles at the cobalt(II) ion clearly indicate a slight distortion away from the ideal tetrahedral geometry.

3.2. Spectroscopy

In the IR spectra, the C–H stretching frequencies of the pyrazolyl groups in complexes **1**, **2** and **3** are at 3101, 3107 and 3105 cm^{-1}, respectively. Complex **1** has a sharp peak at 3489 cm^{-1}, indicative of the O–H stretching of the solvent (CH_3OH). The C=N stretching frequencies in complexes **1**, **2** and **3** are at 1506, 1512 and 1509 cm^{-1}, respectively. All of the absorption spectra of complexes **1** and **2** in acetonitrile are identical,

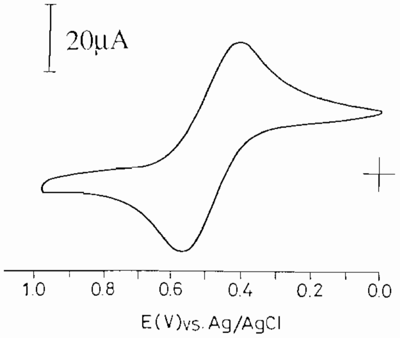

Fig. 4. Cyclic voltammetry for 2.0×10^{-3} M complex **1** in CH_3CN, containing 0.1 M TBAP at room temperature. Scan rate 100 mV s^{-1}.

and the spectra exhibit a copper(II)-to-nitrogen charge-transfer band at 306 nm ($\varepsilon = 3710$ M^{-1} cm^{-1}) and another copper(II)-to-chloride charge-transfer band at 384 nm ($\varepsilon = 2420$ M^{-1} cm^{-1}).

The X-band powder ESR spectra were measured at room temperature. Complexes **1** and **2** both show an axial signal [17] ($g_\parallel = 2.243, g_\perp = 2.112$ for **1** and $g_\parallel = 2.280$, $g_\perp = 2.046$ for **2**). Complex **3** exhibits no ESR signal at room temperature. Nevertheless, there is a very broad isotropic signal at 77 K, and the g value is approximately 3.813.

3.3. Magnetic moments

The magnetic moments were measured at room temperature. The magnetic moments of complex **1** ($\mu_{eff} = 1.85$ BM) can be regarded as normal. The value ($\mu_{eff} = 1.82$ BM per copper) for complex **2** indicates that the bridging $CuCl_2Cu$ unit has no strong magnetic interaction [17]. The magnetic moment of complex **3** ($\mu_{eff} = 4.60$ BM) shows that the tetrahedron cobalt(II) ion (d^7 configuration) is high-spin ($S = 3/2$) [18].

3.4. Electrochemistry

The redox properties of complexes **1** and **2** were studied using cyclic voltammetry (CV). All the CVs for complexes **1** and **2** in acetonitrile are identical. The CV for complex **1** in acetonitrile shows a quasi-reversible wave, of which the $E_{1/2}$ is at 0.49 V versus Ag/AgCl (see Fig. 4). Analysis of the peak current and scan rate by the Randle–Sevcik equation [19] indicates a one-electron transfer for this Cu(II)/Cu(I) redox couple.

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References

[1] F.S. Keij, J.G. Haasnoot, A.J. Oosterling, J. Reedijk, C.J. O'Connor, J.H. Zhang and A.L. Spek, *Inorg. Chim. Acta, 181* (1991) 185.
[2] S.M. Morehouse, A. Polychronopoulou and G.J.B. Williams, *Inorg. Chem., 19* (1980) 3558.
[3] H.M.J. Hendriks, P.J.M.W.L. Birker, G.C. Verschoor and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, (1982) 623.
[4] F. Abraham, M. Lagrenee, S. Sueur, B. Mernari and C. Bremard, *J. Chem. Soc., Dalton Trans.*, (1991) 1433.
[5] (a) N.J. Blackburn, R.W. Strange, A. Farooq, M.S. Haka and K.D. Karlin, *J. Am. Chem. Soc., 110* (1988) 4263; (b) K.D. Karlin, P. Ghosh, R.W. Cruse, A. Farooq, Y. Gultneh, R.R. Jacobson, N.J. Blackburn, R.W. Strange and J. Zubieta, *J. Am. Chem. Soc., 110* (1988) 6769; (c) N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Am. Chem. Soc., 113* (1991) 5664.
[6] (a) T.N. Sorrell, M.L. Garrity and D.J. Ellis, *Inorg. Chim. Acta, 166* (1989) 71; (b) T.N. Sorrell and V.A. Vankai, *Inorg. Chem., 29* (1990) 1687; (c) T.N. Sorrell, V.A. Vankai and M.L. Garrity, *Inorg. Chem., 30* (1991) 207.
[7] F.S. Keij, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk and E. Pedersen, *Inorg. Chim. Acta, 156* (1989) 65.
[8] R.R. Hree, T. Enkoji and J.P. Dailey, *J. Am. Chem. Soc., 79* (1957) 4230.
[9] E.J. Gabe, Y. Le Page, P.S. White and F.L. Lee, *Acta Crystallogr., Sect. A, 43* (1987) S294.
[10] *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, UK, 1974.
[11] W.G. Haanstra, W.A.J.W. van der Donk, W.L. Driessen, J. Reedijk, J.S. Wood and M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, (1990) 3123.
[12] W.G. Haanstra, W.L. Driessen, R.A.G. de Graaff, J. Reedijk, Y.F. Wang and C.H. Stam, *Inorg. Chim. Acta, 186* (1991) 215.
[13] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn and G.C. Verschoor, *J. Chem. Soc., Dalton Trans.*, (1984) 1349.
[14] (a) W.E. Marsh, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem., 21* (1982) 2679; (b) W.E. Marsh, D.S. Eggleston, W.E. Hatfield and D.J. Hodgson, *Inorg. Chim. Acta, 70* (1983) 137; (c) W.E. Marsh, K.C. Patel, W.E. Hatfield and D.J. Hodgson, *Inorg. Chem., 22* (1983) 511.
[15] W.G. Haanstra, W.L. Driessen, J. Reedijk, R. Frohlich and B. Krebs, *Inorg. Chim. Acta, 185* (1991) 175.
[16] J. van Rijn, E. Bouwman, J.R. Empfield, W.L. Driessen and J. Reedijk, *Polyhedron, 8* (1989) 1965.
[17] B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev., 5* (1970) 143.
[18] B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, (1959) 338; B.J. Hathaway and D.G. Holah, *J. Chem. Soc.*, (1964) 2400.
[19] A.J. Bard and L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 1980, p. 218.