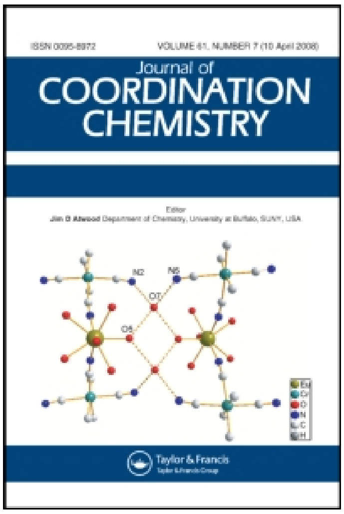

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MIXED-ANION Cu(II) COMPLEXES WITH 3-(PYRIDIN-2-yl)PYRAZOLE (L), SYNTHESES AND X-RAY CRYSTAL STRUCTURE OF $[Cu(L)_2\,Br]ClO_4$ ($L = 3$-(PYRIDIN-2-yl)PYRAZOLE)

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Reaction of the ligand 3-(pyridin-2-yl)pyrazole (L) with $Cu(ClO_4)_2$ and CuX_2 ($X = Cl$, Br, I) gives complexes with stoichiometry $[Cu(L)_2X]ClO_4$ ($X = Cl$, Br, I). The new complexes were characterized by elemental analyses and infrared and electronic spectroscopy. The crystal structure of the $[Cu(L)_2Br]ClO_4$ was determined by X-ray crystallography. The cation complex (i.e. $[Cu(L)_2Br]^+$) contains copper(II) with a distorted trigonal bipyramid geometry with a Br^- ligand occupying an equatorial site. The penta-coordinated metal atom is bonded to two pyridinic nitrogens, two pyrazolic nitrogens, and one bromide anion. The pyrazolic H atoms are hydrogen bonded to Br atoms, resulting in infinite hydrogen-bonded chains running in the *b* direction. There are π–π stacking interactions (charge-transfer arrays) between the parallel aromatic rings belonging to adjacent chains that may help to form hydrogen bonding in the coordination geometry around Cu (II).

Keywords: Copper (II) complexes; Crystal structure; Pyrazole complexes

INTRODUCTION

Research on the coordination chemistry of pyrazole-derived ligands has progressed very rapidly over the last two decades [1–4] with bidentate and tridentate nitrogen hetrocyclic compounds containing six-membered rings such as 2, 2-bipyridine, 1, 10-phenanthroline and 2,2:6,2-terpyridine [5–7]. The incorporation of pyrazole groups in the design of ligands and also preparation of the new mixed-anion complexes allows both electronic and strict control of the properties of metal complexes. A six-membered heterocycle like pyridine and a five-membered heterocycle like pyrazole

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are thus directly linked in a single ligand system [8], because the electronic communication between these two heterocycles can be avoided.

The complexes of the bidentate ligand 3-(pyridin-2-yl)pyrazole have been described elsewhere [9–11], but the mixed-anion complexes of this ligand have seldom been studied.

We recently reported the synthesis and characterization of mixed-anion lead(II) complexes [12–16]. Here, we report the synthesis and characterization of some mixed-anion Cu(II) complexes of the 3-(pyridin-2-yl)pyrazole ligand, $[Cu(L)_2X]ClO_4$ (X = Cl, Br, I).

EXPERIMENTAL

Physical Measurements

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. UV–Vis electronic spectra between 750 and 350 nm, in DMF solution, were run on a Kontron-Uvikon 860.

Synthesis of Ligand

The compound 3-(pyridin-2-yl)pyrazole(L) was synthesized as previously reported [11].

Synthesis of the Complexes

The appropriate metal salt (0.44 mmol: $CuCl_2 \cdot 2H_2O$, 0.074 g; $CuBr_2$, 0.098 g; CuI_2, 0.139 g) and $CuClO_4 \cdot 5H_2O$ (0.44 mmol, 0.155 g) in ethanol (20 mL) was added to a solution of the ligand (1.8 mmol, 0.261 g) in ethanol (20 mL). The resulting solution was stirred at rt for 10 h; powders were obtained which were filtered off dried in vacuum, washed with ethanol–acetonitrile (1:1) and vacuum dried. Green crystals of $[Cu(L)_2Br]ClO_4$ were obtained by slow diffusion of diethyl ether in the methanol solution.

$[Cu(L)_2Cl]ClO_4$: IR (KBr, Cm^{-1}) ν(N–H) 3110; $\nu(C\text{–}H)_{ar}$ 3010; ν(C=C), ν(C=N) 1610, 1580; $\nu(ClO_4)$ 1080; ν(Cu–N) 512; ν(Cu–Cl) 320; ν(Cu–N) 260. UV–Vis: $\lambda_{(\varepsilon)}$(nm) (DMF 1.31×10^{-3} M):800(160). Anal. Calcd. for $C_{16}H_{14}Cl_2CuN_6O_4$(%): C, 39.26; H, 2.86; N, 17.17; Found: C, 39.8; H, 2.95; N, 17.2.

$[Cu(L)_2Br]ClO_4$: IR (KBr, Cm^{-1}) ν(N–H) 3104; $\nu(C\text{–}H)_{ar}$ 3050; ν(C=C), ν(C=N) 1620, 1570; $\nu(ClO_4)$ 1090; ν(Cu–N) 520; ν(Cu–Br) 280; ν(Cu–N) 230. UV–Vis: $\lambda_{(\varepsilon)}$(nm) (DMF 1.31×10^{-3} M):810(200). Anal. Calcd. for $C_{16}H_{14}BrClCuN_6O_4$(%): C, 35.98; H, 2.62; N, 15.74; Found: C, 35.8; H, 2.75; N, 16.1.

$[Cu(L)_2I]ClO_4$: IR (KBr, Cm^{-1}) ν(N–H) 3100; $\nu(C\text{–}H)_{ar}$ 3040; ν(C=C), ν(C=N) 1623, 1578; $\nu(ClO_4)$ 1105; ν(Cu–N) 522; ν(Cu–I) 250; ν(Cu–N) 235. UV-Vis: $\lambda_{(\varepsilon)}$(nm) (DMF 1.31×10^{-3} M): 815(250). Anal. Calcd. for $C_{16}H_{14}ClCuIN_6O_4$(%): C, 33.08; H, 2.41; N, 14.47; Found: C, 33.8; H, 2.65; N, 14.8.

Crystallography

Crystal Data and Refinement Details. $[Cu(L)_2Br]$ ClO_4. $C_{16}H_{14}BrClCuN_6O_4$, M 533.23, monoclinic, Space group $P2_1/c$, a = 9.8616(19), b = 26.981(5), c = 6.8933(13)Å, $\alpha = 90$, $\beta = 90.183(6)$, $\gamma = 90°$, $V = 1834.1(6)$ Å^3, Dc ($Z = 4$ f.u.) 1.931 Mg/m^3, $F(000)$ 1060. Specimen: $0.30 \times 0.2 \times 0.1$ mm; $T_{max,min}$ 0.9281, 0.6374, N 15098, N_0 5325, R 0.0461, R_w 0.1077.

Determination of the Structure. Crystallographic measurements were made at 140(2)K using a Siemens R3 m/V diffractometer. The intensity data were collected within the range. $1.51 \leq \theta \leq 30.03^\circ$ using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collections were obtained from least-squares refinement. Intensities of 15098 unique reflections were measured, from which 5389 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. R, R_w, with goodness of fit on F^2 0.952 are 0.0461, 0.1077. The final difference density map showed a maximum peak and hole of 2.075 and -0.649e Å^{-3}. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the Sadabs programs were applied. All structural calculations were carried out with a PDP – 11/23+ computer using the SDP–PLUS program package [17,18].

Crystal data and structure refinement are given in Table I. Atomic coordinates are given in Table II. Selected bond lengths and angles are given in Table III. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in Figs. 1 and 2.

TABLE I Crystal data and structure refinement for the $[Cu(L)_2Br]ClO_4$

Empirical formula	C_{16} H_{14} Br Cl Cu N_6 C_4
Formula weight	533.23
Temperature	140(2) K
Wave length	0.71073 Å
Crystal system	Monoclinic
space group	$\rho 2_1/c$
Unit cell dimensions	$a = 9.8616(19)$ Å $\alpha = 90^\circ$ $b = 26.981(5)$ Å $\beta = 90.183(6)^\circ$ $c = 6.8933(13)$ Å $\gamma = 90^\circ$
Volume	1834.1(6) Å^3
Z	4
Density (calculated)	1.931 Mg/m^3
Absorption coefficient	3.554 mm^{-1}
$F(000)$	1060
Crystal size	$0.3 \times 0.2 \times 0.1$ mm^3
θ Range for data collection	1.51–30.03°.
Index ranges	$-13 \leq h \leq 13$, $-35 \leq k = 38$, $-9 \leq = l \leq = 6$
Reflections collected	15098
Independent reflections	5325[$R_{int} = 0.0354$]
Completeness to $\theta = 30.03^\circ$	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9281 and 0.6374
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5325/0/262
Goodness-of-fit on F^2	0.952
Final R indices [for 3589 rflns with $I > 2\alpha(I)$	$R_1 = 0.0461$, $wR_2 = 0.1077$
R indices (all data)	$R_1 = 0.0707$, $wR_2 = 0.1171$
Largest diff. peak and hole	2.075 and -0.649e · Å^{-3}

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å \times 10^4$) for [CU(L)$_2$Br]ClO$_4$

Atom	*x*	*y*	*z*	U_{eq}
Br(1)	4677(1)	6144(1)	1906(1)	25(1)
Cu(1)	4873(1)	6326(1)	5694(1)	19(1)
Cl(1)	9334(1)	6137(1)	10358(1)	21(1)
O(1)	9940(3)	5657(1)	10565(4)	40(1)
O(2)	9626(3)	6434(1)	12041(4)	37(1)
O(3)	7909(3)	6089(1)	10130(5)	42(1)
O(4)	9881(2)	6378(1)	8657(4)	27(1)
N(1)	6036(3)	7754(1)	6280(4)	22(1)
C(2)	7322(4)	7599(1)	6718(5)	24(1)
C(3)	7282(3)	7090(1)	6683(5)	22(1)
N(4)	5997(3)	6938(1)	6213(4)	18(1)
C(5)	5261(3)	7349(1)	5984(4)	19(1)
C(6)	3818(3)	7315(1)	5588(5)	19(1)
N(7)	3396(3)	6837(1)	5448(4)	24(1)
C(8)	2084(3)	6750(1)	5062(5)	23(1)
C(9)	1148(4)	7127(1)	4874(5)	26(1)
C(10)	1593(4)	7614(1)	5015(5)	25(1)
C(11)	2941(4)	7711(1)	5348(5)	22(1)
N(12)	3915(3)	4995(1)	7984(4)	22(1)
C(13)	2608(3)	5160(1)	8251(5)	22(1)
C(14)	2578(3)	5640(1)	7623(5)	22(1)
N(15)	3842(3)	5769(1)	6957(4)	19(1)
C(16)	4625(3)	5376(1)	7215(4)	18(1)
C(17)	6050(3)	5400(1)	6712(4)	18(1)
N(18)	6385(3)	5839(1)	5896(4)	19(1)
C(19)	7654(3)	5915(1)	5286(5)	23(1)
C(20)	8652(4)	5566(1)	5605(5)	24(1)
C(21)	8342(4)	5127(1)	6517(5)	25(1)
C(22)	7008(4)	5036(1)	7044(5)	23(1)

TABLE III Selected bond lengths and angles for the [Cu(L)$_2$Br]ClO$_4$

Bond lengths (Å)	*Bond angles* (°)		
Br(1)–Cu(1)	2.6632(7)	N(18)–Cu(1)–N(15)	81.77(11)
Cu(1)–N(18)	1.992(3)	N(18)–Cu(1)–N(7)	177.77(11)
Cu(1)–N(15)	2.013(3)	N(15)–Cu(1)–N(7)	100.46(11)
Cu(1)–N(7)	2.014(3)	N(18)–Cu(1)–N(4)	96.71(11)
Cu(1)–N(4)	2.020(3)	N(15)–Cu(1)–N(4)	144.18(11)
		N(7)–Cu(1)–N(4)	81.40(11)
		N(18)–Cu(1)–Br(1)	89.94(8)
		N(15)–Cu(1)–Br(1)	104.54(8)
		N(7)–Cu(1)–Br(1)	89.64(8)
		N(4)–Cu(1)–Br(1)	111.25(8)

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Properties of the Complexes

Reaction between 3-(pyridin-2-yl)pyrazole (L) and an equimolar mixture of CuX_2 ($X = Cl$, Br, I) and $Cu(ClO_4)_2$ in ethanol solution, provided powdery material analyzing as [Cu(L)$_2$X]ClO$_4$. Isolation of [Cu(L)$_2$X]ClO$_4$ was not successful and each time the 1 : 2 adduct is isolated. The IR spectrum of the solid complex shows $\nu(ClO_4)$ at 1050–1110 cm^{-1} and ν(Cu–Cl), ν(Cu–Br), ν(Cu–I) in 320, 280, 250. Electronic spectra

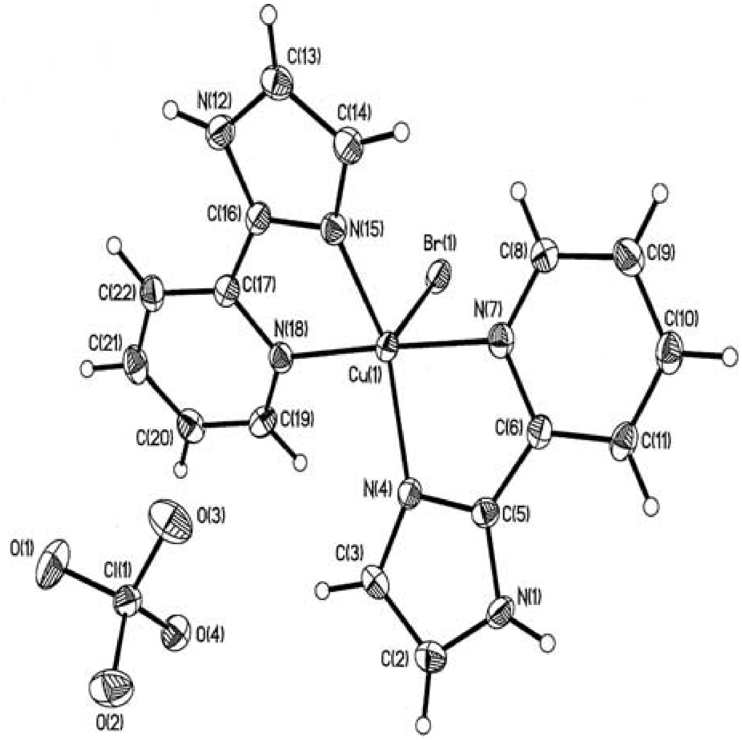

FIGURE 1 ORTEP diagram for $[Cu(L)_2Br]ClO_4$.

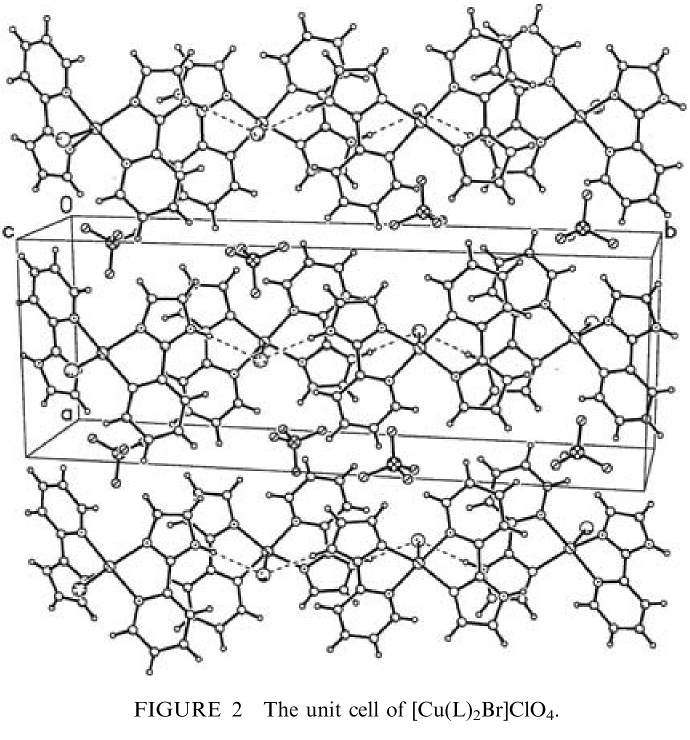

FIGURE 2 The unit cell of $[Cu(L)_2Br]ClO_4$.

TABLE IV Hydrogen bond parameters (distancs [Å] and angles [°]) for $[Cu(L)_2Br]ClO_4$

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(1)–H(1B)···Br(1) [$x, -y+3/2, z+1/2$]	0.88	2.44	3.291	163
N(12)–H(12A)···Br(1) [$-x+1, -y+1, -z+1$]	0.88	2.52	3.373	164

for the synthesized complexes were measured in DMF. The spectra of Cu(II) compounds in DMF solution show one band in the visible region, 970–616 nm ($\varepsilon = 82$–$300\,\mathrm{mol^{-1}\,cm^{-1}l}$). The results did not allow us to infer the geometry of the metal center [19–22].

Crystal Structure of $[Cu(L)_2Br]ClO_4$

The molecular structure of the complex (Fig. 1) consists of discrete $[Cu(L)_2Br]^+$ cations and ClO_4^- anions. The cation complex is mononuclear. Table III lists selected bond distances and angles. In the cation, the metal atom is coordinated to two 3-(pyridin-2-yl)pyrazole (L), *via* one pyrazole nitrogen and one pyridine nitrogen, and to one Br^- anion. 3-(pyridin-2-yl)pyrazole (L) behaves as a bidentate ligand and uses only two of their three donor nitrogen atoms, forming a five-membered metalacycle.

The coordination around Cu is a distorted trigonal bipyramid. The bond distances Cu–N_{py} (1.992, 2.014 Å) and Cu–N_{pz} (2.013, 2.020 Å) are consistent with previously described values (1.996, 2.092 Å) and (1.929, 2.056 Å) [23–26]. The bite angles of N(18)–Cu(1)–N(15) and N(7)–Cu(1)–N(4), 81.77 and 81.40° are similar to those reported [27–29]. The ligand L is not completely planar. The pyridyl group are slightly twisted with respect to the pyrazole. The angles between rings are: N(4)–C(5)–C(6)–N(7) = 1.6, N(1)–C(5)–C(6)–N(7) = 177.6, N(15)–C(16)–C(17)–N(18) = 3.7, and N(12)–C(16)–C(17)–N(18) = 177.4 Å.

Cations are linked by hydrogen bonding. The coordinated 3-(pyridin-2-yl)pyrazole (L) molecule is involved in hydrogen bonding acting as hydrogen-bond donors with coordinated Br atoms as potential hydrogen-bond acceptors. The hydrogen bond parameters {distances [Å], d(D–H), d(H···A), d(D···A), and angles [°], <(DHA)} are given in Table IV. As shown in Fig. 2, hydrogen bonding yields infinite chains parallel to the crystallographic vector *b*. Each cation is bonded to two neighbors. Both amine H atoms are hydrogen bonded to Br atoms.

The strikingly different feature of this compound to those reported [9–11] is that, there is a π–π stacking interaction (charge-transfer arrays) [30,31] between the parallel aromatic rings from adjacent chains, as shown in Fig. 2. As planar species in which the mean molecular planes are close to parallel and separated by a distance of ~3.5 Å, close to that of the planes in graphite. Whether the π–π stacking between the parallel aromatic rings help to form hydrogen bonding in coordination geometry around the metal ion, or hydrogen bonding helps to form π–π stacking is an open question.

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B.A. degree at the University of the Peyame Noor. We thank the Institute of Organoelement Compounds of the Russian Academy of Science for determining the crystal structure by X-ray crystallography.

Supplementary Material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited at Cambridge Crystallography Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition numbers for this compound 178445.

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