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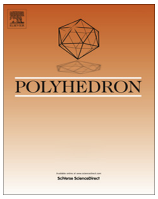

Crystal structures and magnetic properties of two-dimensional copper(II) complexes bridged with pyrazine-2-carboxamide

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ABSTRACT

A variety of $[Cu(pyza)_2](X)_2$ (X = BF_4 (**1**), ClO_3 (**2**), ClO_4 (**3**), PF_6 (**4**), AsF_6 (**5**)) were synthesized (pyza = pyrazine-2-carboxamide). The crystal structures of **1**–**5** have been determined to be isomorphous to that of known **3** in a monoclinic $P2_1/c$ space group. They form a quadratic copper(II) array with pyza bridges. The 1- and 4-nitrogen atoms in the pyrazine ring are coordinated to copper ions at equatorial and axial positions, respectively. Complexes **1**–**5** showed very weak antiferromagnetic interactions with $J/k_B = -0.439(6)$, $-0.321(5)$, $-0.304(1)$, $-0.209(3)$, and $-0.264(5)$ K, respectively, analyzed on the basis of an antiferromagnetic two-dimensional model. The magnitude of J almost correlates with the Cu···Cu distance and the cell volume.

1. Introduction

We are interested in pyrazine-bridged copper(II) complexes showing ferromagnetic coupling [1], which may be an apparent violation of the spin-polarization scheme [2], but would be feasible with an appropriate molecular design such as Cu(equatorial)–pyz–Cu(axial) (Fig. 1). Given the octahedron or square pyramid of $3d^9$ Cu^{2+} coordination structures, the magnetic orbital $3d_{x^2-y^2}$ is located on a basal plane. The orthogonal arrangement between magnetic orbitals is crucial for pursuing ferromagnetic coupling, and Anderson, Goodenough, and Kanamori explained the magneto-structure relation with the mutual direction of the magnetic orbitals of M and the lone-pair orbitals of X in M–X–M systems [3]. This theory can be extended to pyrimidine- and pyrazine-bridged coordination compounds [4]. Thus, the constructing the copper complexes having a Cu(equatorial)–pyz–Cu(axial) motif is a target of novel high-spin species.

Pyrazine-2-carboxamide (pyza) is known as an antitubercular agent [5] and sometimes called as pyrazinamide or PZA. Various coordination compounds involving pyza are known [6], where the role of a bridging ligand between Cu ions is highlighted [7]. The two-dimensional (2-D) grid polymer $[Cu(pyza)_2](ClO_4)_2$ has been known since 1973 [8], and it has a repeating Cu(equatorial)–pyz–Cu(axial) coordination mode. Unfortunately, it has been reported to exhibit weak antiferromagnetic interaction [9]. We moved to study the crystal structures and magnetic properties of related Cu–pyza compounds. We prepared a variety of 2-D grid polymers $[Cu(pyza)_2](X)_2$, the magnetic properties of which are tunable by the size of the counter anion X in the isomorphous series. A systematic study will be developed after the magnetic and structural analyses are combined.

2. Results and discussion

2.1. Synthesis and IR-spectroscopic characterization

Five compounds of $[Cu(pyza)_2](X)_2$ (X = BF_4 (**1**), ClO_3 (**2**), ClO_4 (**3**), PF_6 (**4**), AsF_6 (**5**)) were synthesized. Compound **3** has been known, and the preparation of **1** and **3** is highly reproducible according to the known procedure [8,9]. We have found that using $Cu(CF_3SO_3)_2$ or $CuSO_4$ gave no 2-D grid compounds, and accordingly $Cu(CF_3SO_3)_2$ was utilized as a starting copper ion source when commercially unavailable copper salts are applied to the present synthetic procedure. Namely, mixing $Cu(CF_3SO_3)_2$ and appropriate anions (ClO_3^-, PF_6^-, and AsF_6^-) in the presence of a stoichiometric amount of pyza in water or methanol gave anion-exchanged 2-D compounds (**2**, **4**, and **5**, respectively). They were obtained as light-blue platelet crystals, and could be subjected to elemental, structural, and magnetic analyses without further purification. We tried to prepare an SbF_6^- 2-D grid compound in order to compare with PF_6^- and AsF_6^- 2-D grid ones. However, preparation of $[Cu(pyza)_2](SbF_6)_2$ was unsuccessful under the conditions described above.

The elemental analysis suggests that the proposed composition. Finally, the crystal structures of **1**–**5** have been determined by means of X-ray diffraction studies (Section 2.2). The IR spectroscopic study is compatible with the present molecular and crystal structures. Complexes **1**, **2**, **4**, and **5** were characterized by asymmetric OCN (ν_{as}(OCN)) and symmetric OCN ((ν_s(OCN)) stretching

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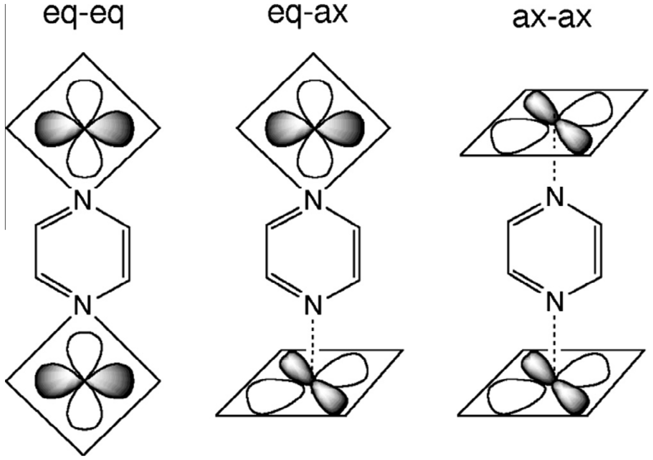

Fig. 1. Coordination geometries of Cu-μ-pyz-Cu systems.

bands according to the assignments of **3** [6a]. The v_{as}(OCN) and v_s(OCN) were observed in the regions 1693–1681 and 1411–1407 cm^{-1}, respectively. The N–H stretching bands (v (N–H)) were found in the region 3598–3086 cm^{-1}. A few v (N–H) bands shifted to a lower frequency are assigned to N–H···F hydrogen bonds in **1**, **4**, and **5**, and N–H···O hydrogen ones in **2** and **3** (see Sections 2.2 and 4.2).

2.2. Crystallographic analysis

The crystal structures of **1**–**5** determined by the X-ray diffraction study. Selected crystallographic data are listed in Table 1. The molecular and crystal structure of **1** is shown in Fig. 2. The coordination geometry of Cu ion is an elongated octahedral (Oh) type. The Cu1–N1 and Cu1–N2^{ii} bond lengths are 1.988(3) and 2.459(4) Å, respectively. The ax Cu1–N2^{ii} distance is considerably long, and is comparable with those of the 1-D $[Cu(hfac)_2(\mu\text{-}L)]_n$ (L = non-substituted and substituted pyrazines) (2.408(2)–2.602(2) Å) [1,10,11]. The equatorial positions are occupied by two oxygen atoms, which are situated *trans* to each other. The eq Cu1–O1 distance (1.953(3) Å) is somewhat shorter than eq Cu1–N1 one. Consequently, this compound has an eq-ax-type pyrazine bridge in the 2-D grid polymer.

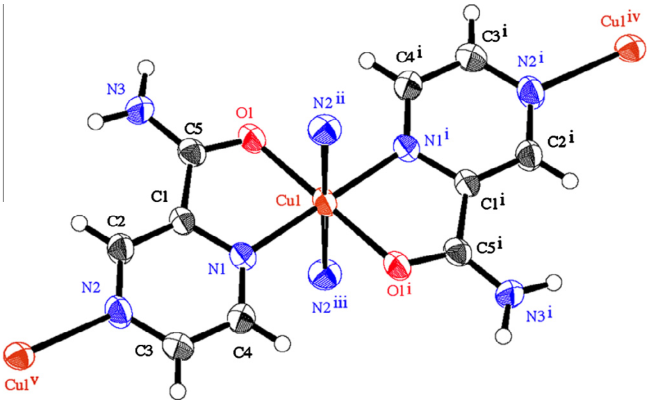

Fig. 2. Ortep drawing of the cationic moiety of **1**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operation codes of i, ii, iii, iv, and v are (1 − *x*, −*y*, 1 − *z*), (+*x*, 1/2 − *y*, −1/2 + *z*), (1 − *x*, −1/2 + *y*, 3/2 − *z*), (1 − *x*, −1/2 + *y*, 1/2 − *z*), and (1 − *x*, 1/2 + *y*, 3/2 − *z*), respectively.

The Cu ion has a distorted Oh structure, which seems to be crucial for the orthogonal arrangement of the magnetic orbitals. The bond angle of N1–Cu1–N2^{ii} in **1** is 88.84(11)° around the ideal angle of 90°, while those of O1–Cu1–N1 and O1–Cu1–N2^{ii} deviate from the right angle (Table 2). Further, the basal Cu1–N1–C1–C4 plane is appreciably pyramidalized, similarly to that of the 2-substitued-pyrazine bridged copper(II) complexes [1,14].

Compounds **1**–**5** are all isomorphous to that of known **3** in a monoclinic $P2_1/c$ space group, regardless of the anion shape (trigonal pyramid, tetrahedron, or octahedron). The cell volumes are 829.39(13)–965.66(17) $Å^3$, depending on the anion size. The size of anions is found to be crucial for the 2-D grid formation. The evaluated volumes of the anions using quantum-chemical calculations are as follows: BF_4 (53.4 $Å^3$), ClO_4 (54.4 $Å^3$), PF_6 (73.0 $Å^3$), AsF_6 (78.5 $Å^3$), SbF_6 (88.7 $Å^3$), and CF_3SO_3 (86.9 $Å^3$) [15]. The relatively large anions such as SbF_6 and CF_3SO_3 gave no 2-D grid polymers (Section 2.1). Thus, a critical volume of anions forming 2-D grids is located between those of AsF_6 and SbF_6 (or CF_3SO_3) anions.

The 2-D grid structures of **1**, **2**, and **5** are shown in Fig. 3(a)–(c), respectively. The infinite 2-D polymer is located parallel to the crystallographic *bc* plane. Because of the similarity of the tetragonal counter anions, it is reasonable that **1** and **3** are isostructural. Interestingly, **2** having a trigonal pyramid anion with a lower

Table 1
Selected crystallographic data for **1**–**5**.

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$C_{10}H_{10}B_2CuF_8N_6O_2$	$C_{10}H_{10}Cl_2CuN_6O_8$	$C_{10}H_{10}Cl_2CuN_6O_{10}$	$C_{10}H_{10}CuF_{12}N_6O_2P_2$	$C_{10}H_{10}As_2CuF_{12}N_6O_2$
Formula weight	483.38	476.68	508.68	599.70	687.60
Habit	blue platelet	blue platelet	blue platelet	blue platelet	blue platelet
Dimension (mm^3)	0.30 × 0.30 × 0.04	0.30 × 0.25 × 0.07	0.35 × 0.35 × 0.10	0.75 × 0.55 × 0. 07	0.35 × 0.30 × 0.01
T (K)	296	296	296	296	296
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	8.6588(7)	8.8803(18)	8.784(3)	9.3414(9)	9.5711(12)
b (Å)	9.8389(9)	9.7459(13)	9.968(3)	10.0460(9)	10.0899(8)
c (Å)	10.3610(10)	10.4849(16)	10.421(2)	10.6311(10)	10.6233(9)
β (°)	110.012(2)	111.786(6)	110.604(8)	109.297(3)	109.733(4)
V ($Å^3$)	829.39(13)	842.6(3)	854.0(4)	941.61(16)	965.66(17)
Z	2	2	2	2	2
D_{calc} (g cm^{-3})	1.935	1.879	1.978	2.115	2.365
μ (Mo Kα) (mm^{-1})	1.425	1.669	1.662	1.470	4.670
Unique data	1883	1902	1928	2116	2196
$R(F)^a$ ($I > 2\sigma(I)$)	0.0487	0.0545	0.0488	0.0648	0.0549
R_w $(F^2)^b$ (all data)	0.0691	0.0770	0.0594	0.0844	0.0628

[a] $R = \Sigma\, ||F_o| - |F_c|| / \Sigma |F_o|$ (unit weights).
[b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.