Note

# Dinuclear copper(II) chloro complex of the ligand 2,3,5,6-tetra(2-pyridyl)pyrazine

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## Abstract

Crystallographic and magnetic studies have been performed on the complex, $[\{CuCl\}_2(\mu\text{-tppz})][PF_6]_2$, where tppz is 2,3,5,6-tetra-2-pyridinylpyrazine. The crystal structure revealed an infinite, ionic chain wherein Cu(II) ions are respectively above and below the plane of the pyrazine moiety of the bridging tppz ligand with the pyridine moieties moving out of the pyrazine plane in order to coordinate to Cu(II). Each chloride ligand bonds equatorially to Cu(II) in a $[\{CuCl\}_2(\mu\text{-tppz})]^{2+}$ ion and axially to a neighboring $[\{CuCl\}_2(\mu\text{-tppz})]^{2+}$ ion so as to form a one-dimensional chain in the solid state. The temperature-dependent magnetic susceptibility could be satisfactorily fitted by using a modified Bleaney–Bowers expression (for $H = -JS_a \cdot S_b$ $J = -5.6$ cm$^{-1}$ and $g = 2.16$) where the exchange interaction is suggested to involve the orbitals of the tppz ligand.
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## 1. Introduction

A number of researchers have investigated transition metal complexes of 2,3,5,6-tetra-2-pyridinylpyrazine tppz because of its application to supramolecular materials with desirable photophysical [1] or magnetic [2–4] properties. While both Cu(II) mononuclear [5] and dinuclear [3] complexes have been characterized, they involve complexes in which the copper ion's coordination sphere is either six-coordinated or contains two single-atom, anion ligands. In both cases, the possibility of forming extended arrays of linked dinuclear complexes in the solid state is diminished.

We now report the preparation, crystallography and magnetic characterization of $[\{CuCl\}_2(\mu\text{-tppz})][PF_6]_2$, a complex which forms a one-dimensional chain in the solid state.

## 2. Experimental

### 2.1. Preparation of $[\{CuCl\}_2(\mu\text{-tppz})][PF_6]_2$

A solution of $CuCl_2 \cdot n H_2O$ (0.269 g) and 2,3,5,6-tetra-2-pyridinylpyrazine (tppz) (0.388 g) in 50 mL dimethylformamide was heated at 60 °C for 24 h. The brown-green precipitate which formed was collected and washed with acetone and ether. This product was dissolved in water and precipitated from solution as a hexafluorophosphate salt by the addition of $NH_4PF_6$. The product was collected, washed with cold water and ether, and then air dried. The crude product was purified by column chromatography (alumina grade III, weakly acidic, 150 mesh with column dimensions:

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height 40 cm and diameter 3 cm). Elution with 3:1 tolu-ene:acetonitrile gave a light green band which is sug-gested to be a dimethylformide copper complex by its IR spectrum. Elution with acetonitrile gave the major product, a green band, which was collected and the sol-vent removed. Diffusion of ether into an acetonitrile solution of the complex gave dark green crystals suitable for crystallography (0.65 g, 74%). *Anal.* Calc. For $C_{24}H_{16}Cl_2Cu_2F_{12}N_6P_2$: C, 32.89; H, 1.84; N, 9.59. Found: C, 32.96; H, 1.86; N, 9.54%.

### 2.2. Crystallography

Crystal data and structure refinement details are re-ported in Table 1. A suitable crystal was selected and mounted on a glass fiber with viscous oil and cooled to the data collection temperature. The data were col-lected on a Bruker-AXS SMART 1K CCD using an $\omega$-scan technique and corrected for absorptions using equivalent reflections [6]. Unit cell parameters were ob-tained from 60 data frames, 0.3° $\omega$, from three different sections of the Ewald sphere. Unit cell parameters and systematic absences in the diffraction data were consist-ent with space groups *C2*, *Cm*, and *C2/c*. Solution in the centric space group option yielded chemically reasona-ble and computationally stable results of refinement. The structure was solved by direct methods and refined with full-matrix least-squares procedures. The ionic, infinite chain is located on a mirror plane and propa-

gated by a twofold rotation perpendicular to the mirror. Anisotropic refinement was performed on all non-hy-drogen atoms. All hydrogen atoms were calculated. Scattering factors are contained in the SHELXTL 6.12 program library [6]. The CIF is available from the Cam-bridge Crystallographic Data Center under the deposi-tary number CCDC 249298.

## 3. Results and discussion

The synthesis of $[\{CuCl\}_2(\mu\text{-tppz})][PF_6]_2$ was achieved by the metathesis of the loosely-held chloride ions of $[\{CuCl_2\}_2(\mu\text{-tppz})]$ with $NH_4PF_6$ in aqueous solution. The hexafluorophosphate complex is readily soluble in polar organic solvents and, after purification by chromatography using alumina and recrystallization from acetonitrile/ether solution, was isolated as dark green crystals in 74% yield. The complex appeared stable in solution for days at a time and no evidence of decom-position was seen in the solid state.

A crystallographic analysis of $[\{CuCl\}_2(\mu\text{-tppz})][PF_6]_2$ was performed on a single crystal and the results have been compiled in Table 1. Selected bond lengths and bond angles as well as ORTEP and unit cell drawings appear in Figs. 1 and 2. The ORTEP drawing of the complex cation (Fig. 1) shows identical tetrago-nally distorted coordination spheres of nitrogen and chloride donor atoms about the Cu(II) ions. The two Cu(II) ions are, respectively, above and below the plane of the pyrazine moiety of the bridging tppz ligand with

Table 1
Crystal data and structure refinement for $[\{CuCl\}_2(\mu\text{-tppz})][PF_6]_2$

| Empirical formula | $C_{24}H_{16}Cl_2Cu_2F_{12}N_6P_2$ |
|---|---|
| Formula weight (g/mol) | 876.35 |
| Temperature (K) | 203(2) |
| $\lambda$Mo K$\alpha$ (Å) | 0.71073 |
| Crystal system | monoclinic, |
| Space group | *C2/m* |
| *Unit cell dimensions* | |
| $a$ (Å) | 13.314 (3) |
| $b$ (Å) | 12.901 (2) |
| $c$ (Å) | 8.9039 (17) |
| $\beta$ (°) | 99.260 (4) |
| Volume (Å³) | 1509.4 (5) |
| $Z$, $Z'$ | 8, 0.25 |
| Calculated density (g/cm³) | 1.928 |
| Absorption coefficient (mm⁻¹) | 1.796 |
| $F(000)$ | 864 |
| Crystal size (mm) | $0.10 \times 0.10 \times 0.10$ |
| $\theta$ Range (°) | 2.21–28.47 |
| Reflections collected/unique | 3828/1805 [$R_{int} = 0.0416$] |
| $T_{min}/T_{max}$ | 0.817274 |
| Data/restraints/parameters | 1805/0/121 |
| Goodness-of-fit on $F^2$ | 1.049 |
| $R(F)$ [$I > 2\sigma$] (%) | 4.16 |
| $R(wF^2)$ (%)[a] | 10.65 |

[a] Quantity minimized $= R(wF^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(wF_o^2)^2\}^{1/2}$: $R(F) = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$ : $w = [\sum^2(F_o^2) + (aP)^2 + bP]^{-1}$ $P = [2F_c^2 + \text{Max}(F_o, 0)]/3$.
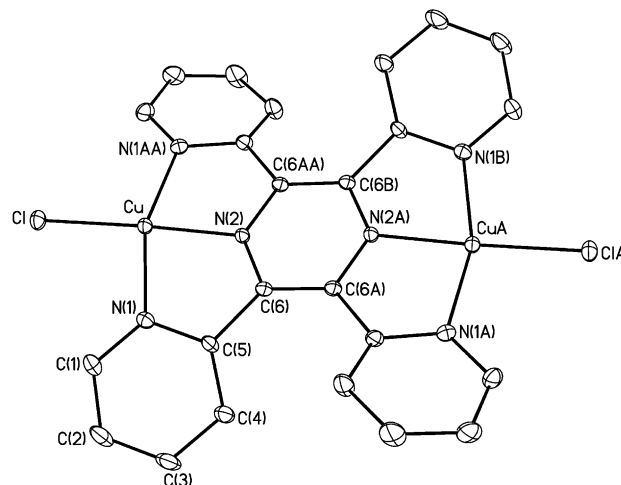


Fig. 1. ORTEP of the complex, $[\{CuCl\}_2(\mu\text{-tppz})][PF_6]_2$, the hydrogen atoms and counter anions have been excluded for clarity. Ellipsoids are depicted at 30% probability. Selected bond lengths (Å) and bond angles (°): Cu–N(2), 1.977(3); Cu–N(1AA), 2.038(3); Cu–N(1), 2.038(3); Cu–Cl, 2.2431(12); N(2)–Cu–N(1AA), 80.16(7); N(2)–Cu–N(1), 80.16(7); N(1AA)–Cu–N(1), 159.00(15); N(2)–Cu–Cl, 174.85(10); N(1AA)–Cu–Cl, 99.47(7); N(1)–Cu–Cl, 99.47(7); C(1)–N(1)–Cu, 126.0(2); C(5)–N(1)–Cu, 113.46(19).