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## A copper(II)–pyrazole complex cation with $\bar{3}$ imposed symmetry

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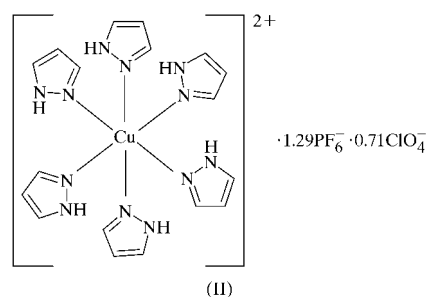
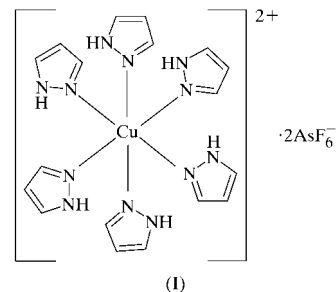
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The reaction of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaAsF}_6$  and excess pyrazole yields hexakis(pyrazole- $\kappa N^2$ )copper(II) bis(hexafluoroarsenate),  $[\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_6](\text{AsF}_6)_2$  or  $[\text{Cu}(\text{pzH})_6](\text{AsF}_6)_2$  (pzH is pyrazole), (I). The analogous hexakis(pyrazole- $\kappa N^2$ )-copper(II) hexafluorophosphate perchlorate complex,  $[\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_6](\text{PF}_6)_{1.29}(\text{ClO}_4)_{0.71}$  or  $[\text{Cu}(\text{pzH})_6](\text{PF}_6)_{1.29}(\text{ClO}_4)_{0.71}$ , (II), is obtained in a similar fashion, using  $\text{KPF}_6$  in place of  $\text{NaAsF}_6$ . Both compounds contain the hitherto unknown  $[\text{Cu}(\text{pzH})_6]^{2+}$  complex cation, in which the copper(II) ion lies at the center of a regular octahedron of coordinated N atoms. The cation has crystallographically imposed  $\bar{3}$  symmetry. The X-ray data indicate that the lack of the expected distortion can be accounted for by the presence of either static Jahn–Teller disorder or dynamic Jahn–Teller distortion.

### Comment

Pyrazole (pzH) forms a variety of metal complexes (Steel, 1990; Trofimenko, 1986, 1972), the simplest having the formulation  $[\text{M}(\text{pzH})_n]\text{X}_p$ , where  $M$  is a metal and  $X$  is an anion. Reported complexes with  $n = 6$  include  $[\text{M}(\text{pzH})_6]\text{X}_2$ , with  $M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}$  or  $\text{Cd}$ , and  $X = \text{NO}_3, \text{BF}_4$  or  $\text{ClO}_4$  (Trofimenko, 1972). The structures of  $[\text{Ni}(\text{pzH})_6](\text{BF}_4)_2$  (Ten-Hoedt *et al.*, 1983),  $[\text{Ni}(\text{pzH})_6](\text{NO}_3)_2$  (Reimann *et al.*, 1970) and  $[\text{Mn}(\text{pzH})_6](\text{ClO}_4)_2$  (Lumme *et al.*, 1988) are known. Thus, hexakis(pyrazole) complexes exist for all first-row divalent transition metal ions from Mn to Zn, except for Cu. It has been suggested that a maximum of four pyrazoles can coordinate to  $\text{Cu}^{\text{II}}$  (Trofimenko, 1972; Nicholls & Warburton, 1971; Daugherty & Swisher, 1968). We attribute this lack of maximal coordination to the tendency of six-coordinate  $\text{Cu}^{\text{II}}$  complexes to undergo Jahn–Teller distortions (Hathaway & Billing, 1970). Such distorted structures are, presumably, more likely to form with six non-equivalent ligands. Hence, we anticipated that six pyrazoles could coordinate to  $\text{Cu}^{\text{II}}$  if non-coordinating anions were used and, therefore, undertook the

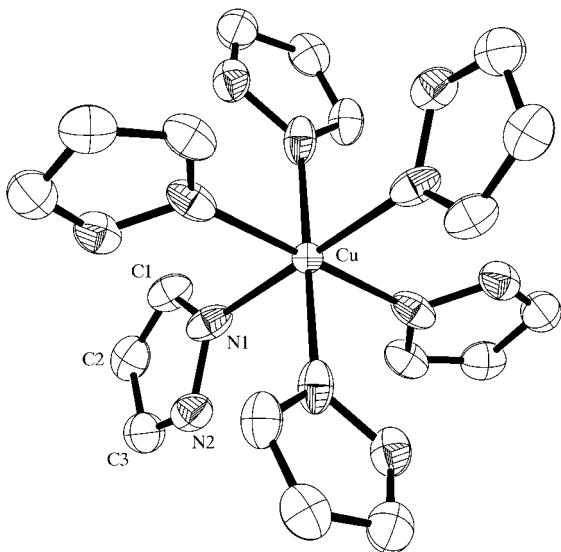
preparation of hexakis(pyrazole)copper(II) complexes using weakly ligating  $\text{AsF}_6^-$  and  $\text{PF}_6^-$  as the counter-ions. We have isolated two isostructural salts containing the  $[\text{Cu}(\text{pzH})_6]^{2+}$  complex cation, namely  $[\text{Cu}(\text{pzH})_6](\text{AsF}_6)_2$ , (I), and  $[\text{Cu}(\text{pzH})_6](\text{PF}_6)_{1.29}(\text{ClO}_4)_{0.71}$ , (II), and their crystal structures are presented here.



The  $\text{Cu}^{\text{II}}$  atoms in (I) (Fig. 1 and Table 1) and (II) (Fig. 2 and Table 2) occupy sites with  $\bar{3}$  symmetry, requiring symmetry-equivalent Cu–N bonds. Such equal copper–ligand bond distances are atypical for  $\text{Cu}^{\text{II}}$  and warrant further discussion. Six-coordinate  $\text{Cu}^{\text{II}}$  complexes tend to have distorted octahedral geometries, usually with two long axial bonds and four short equatorial bonds, in accordance with the Jahn–Teller theorem (Hathaway & Billing, 1970; Ham, 1962). Few compounds have been reported in which the symmetry of the Cu coordination polyhedron is higher than that allowed by the Jahn–Teller theorem. These include  $[\text{Cu}(\text{H}_2\text{O})_6](\text{BrO}_3)_2$  (Blackburn *et al.*, 1991) and  $[\text{K}_2\text{Pb}(\text{Cu}(\text{NO}_2)_6)]$  (Isaacs & Kennard, 1967), which contain monodentate ligands,  $[\text{Cu}(\text{en})_3](\text{SO}_4)$  (en is ethylenediamine; Cullen & Lingafelter, 1970), which contains three bidentate ligands, and  $[\text{Cu}(\text{ompa})_2](\text{ClO}_4)_2$  (ompa is octamethylpyrophosphoramidate; Joesten *et al.*, 1968, 1970) and  $[\text{Cu}(\text{tach})_2](\text{NO}_3)_2$  (tach is *cis,cis*-1,3,5-triaminocyclohexane; Ammeter *et al.*, 1979), which contain two tridentate ligands.

One explanation of these apparent violations of the Jahn–Teller theorem is the existence of a dynamic Jahn–Teller distortion, *i.e.* the complex could oscillate between three possible distortions, giving a regular time average. A second possibility is disordered static Jahn–Teller distortion, in which each molecule is trapped in a single distortion, and these distortions in turn are distributed randomly to produce a spatial average.

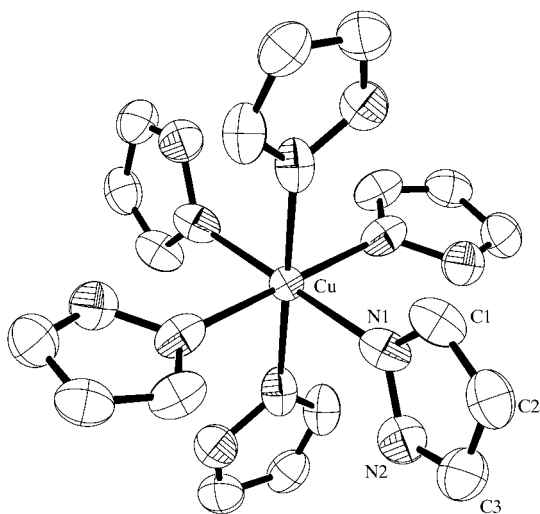
Evidence in support of Jahn–Teller effects in (I) and (II) is provided by the direction of the maximum anisotropic displacement parameter of each bonded N atom (Figs. 1 and 2), which is nearly parallel to the metal–N bond (Cullen &



**Figure 1**

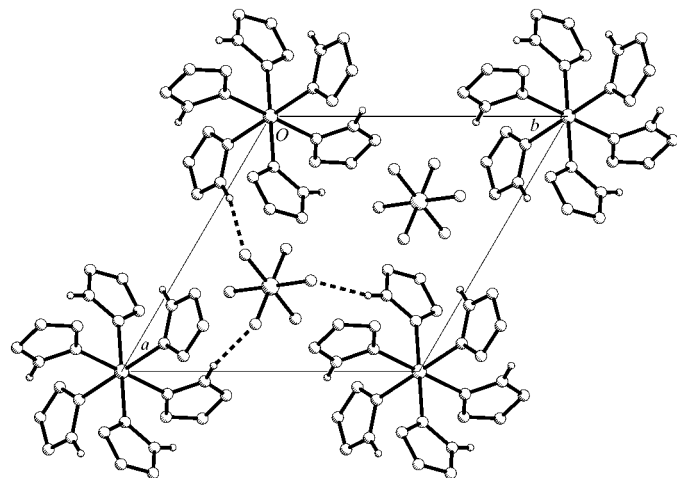
A view of the structure of the cation of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Lingafelter, 1970; Blackburn *et al.*, 1991). The angle between the largest principle axis of the displacement ellipsoid and the metal–N1 bond is  $23.5^\circ$  in (I) and  $26.2^\circ$  in (II). In contrast, a much larger angle ( $49.5^\circ$ ) is observed for the isomorphous Ni<sup>II</sup> complex,  $[\text{Ni}(\text{pzH})_6](\text{NO}_3)_2$ , which is not subject to Jahn–Teller effects. These effects are also quantifiable in terms of  $\Delta U$  values (Chandrasekhar & Bürgi, 1984). For compounds (I) and (II), the  $\Delta U$  values along the Cu–N1 bonds are  $0.0323$  and  $0.0324 \text{ \AA}^2$ , respectively. These are roughly an order of magnitude larger than the  $\Delta U$  values for the other bonded pairs of atoms in the pyrazole ring in both (I) and (II). They



**Figure 2**

A view of the structure of the cation of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.



**Figure 3**

A packing diagram for (I) projected down the *c* axis, with the hydrogen-bonding interactions shown as dashed lines. The As atom sits on the threefold axis in  $P\bar{3}$ , resulting in two sets of (three) non-equivalent F atoms, only one set of which is involved in hydrogen bonding.

are also relatively larger than the value of  $0.0105 \text{ \AA}^2$  obtained for  $\Delta U$  along the Ni–N1 bond in  $[\text{Ni}(\text{pzH})_6](\text{NO}_3)_2$ .

Hydrogen bonds in (I) and (II) create an extended network of  $[\text{Cu}(\text{pzH})_6]^{2+}$  and  $\text{AsF}_6^-$  or  $\text{PF}_6^-$  moieties. For example, as illustrated in Fig. 3, the N–H H atom of each pyrazole ring in (I) forms a hydrogen bond to an F atom of the  $\text{AsF}_6^-$  ion [ $\text{H}2 \cdots \text{F}1 = 2.074(3) \text{ \AA}$ ]. Each  $\text{AsF}_6^-$  anion forms hydrogen bonds to three different  $[\text{Cu}(\text{pzH})_6]^{2+}$  moieties, and each  $[\text{Cu}(\text{pzH})_6]^{2+}$  moiety forms hydrogen bonds to six different  $\text{AsF}_6^-$  anions.

The magnetic moment and visible spectrum data for (I) and (II) (see *Experimental*) are characteristic of a magnetically dilute six-coordinate Cu<sup>II</sup> ion. The energy of the peak maximum in the visible spectra ( $15\,100 \text{ cm}^{-1}$ ) is comparable with those observed for other complexes containing the  $[\text{CuN}_6]^{2+}$  chromophore (McKenzie, 1970). The IR bands for the  $\text{PF}_6^-$  and  $\text{AsF}_6^-$  moieties are assigned on the basis of data from previously characterized hexafluorophosphate and hexafluoroarsenate complexes (Morrison & Thompson, 1982). For (I),  $\nu_3$  and  $\nu_4$  of the  $\text{AsF}_6^-$  group are observed at  $705$  and  $411 \text{ cm}^{-1}$ , respectively, and show no splitting. The corresponding bands for the  $\text{PF}_6^-$  group in (II) are observed at  $840$  and  $561 \text{ cm}^{-1}$ , respectively. These data are consistent with criteria for non-coordinating  $\text{AsF}_6^-$  or  $\text{PF}_6^-$  moieties (Morrison & Thompson, 1982).

## Experimental

To prepare compound (I), a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $0.849 \text{ g}$ ,  $2.29 \text{ mmol}$ ) in ethanol ( $5 \text{ ml}$ ) containing 10% *v/v* 2,2-dimethoxypropane was added to  $\text{NaAsF}_6$  ( $0.961 \text{ g}$ ,  $4.54 \text{ mmol}$ ) dissolved in the same solvent ( $30 \text{ ml}$ ). The mixture was stirred for 15 min and filtered. To the filtrate was added more  $\text{NaAsF}_6$  ( $0.500 \text{ g}$ ,  $2.36 \text{ mmol}$ ), and the mixture was once again stirred for 15 min and then filtered into a solution of pyrazole ( $1.00 \text{ g}$ ,  $14.7 \text{ mmol}$ ) in the above solvent ( $4 \text{ ml}$ ).

The mixture was stirred for 30 min, after which the solvent was pumped off under vacuum. The blue solid product was recrystallized from methanol. Blue crystals of (I) were obtained after about 2 d. Crystals for X-ray analysis were removed directly from the supernatant liquid. The rest of the product was isolated by decantation, washed with small amounts of methanol and dried in a desiccator containing Drierite. Analysis found: C 25.81, H 2.91, N 19.29%;  $C_{18}H_{24}As_2CuF_{12}N_{12}$  requires: C 25.44, H 2.85, N 19.78%. Spectroscopic data: visible ( $\lambda_{max}$ , nm, MeOH): 664;  $\epsilon$  ( $dm^3 mol^{-1} cm^{-1}$ ): 33; IR ( $\nu$ ,  $cm^{-1}$ ,  $AsF_6^-$ ): 705 ( $\nu$  s), 411 (s);  $\mu_{eff}/BM$  (296 K) 1.90.

Compound (II) was prepared following the same procedure as for (I), using  $Cu(ClO_4)_2 \cdot 6H_2O$  (0.823 g, 2.22 mmol),  $KPF_6$  (0.830 g, 4.51 mmol, then 0.485 g, 2.64 mmol) and pyrazole (1.098 g, 16.1 mmol). The  $KPF_6$ , however, only partially dissolved in the solvent. Analysis found: C 28.37, H 3.14, N 21.94%;  $C_{18}H_{24}CuF_{12}N_{12}P_2$  requires: C 28.37, H 3.17, N 22.06%. Spectroscopic data: visible ( $\lambda_{max}$ , nm, MeOH): 663;  $\epsilon$  ( $dm^3 mol^{-1} cm^{-1}$ ): 34; IR ( $\nu$ ,  $cm^{-1}$ ,  $PF_6^-$ ): 840 ( $\nu$  s), 561 (s);  $\mu_{eff}/BM$  (296 K) 1.91. The crystal of (II) used for X-ray analysis contained roughly one-third  $ClO_4^-$  ions. This was not characteristic of the bulk sample, for which elemental analysis and IR data indicate minimal, if any,  $ClO_4^-$ .

Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana. IR spectra were recorded as KBr pellets on a Bio-Rad FTS3000 FT-IR spectrometer. Visible spectra were recorded on a Cary 1C UV-Visible spectrophotometer. Magnetic measurements were made at room temperature on a Johnson-Matthey MKI magnetic susceptibility balance.

## Compound (I)

### Crystal data

$[Cu(C_3H_4N_2)_6](AsF_6)_2$   
 $M_r = 849.87$   
 Trigonal,  $P\bar{3}$   
 $a = 10.1780$  (14) Å  
 $b = 10.1780$  (14) Å  
 $c = 8.0980$  (16) Å  
 $V = 726.5$  (2) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 1.943$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 3793 reflections  
 $\theta = 1.0$ – $27.5^\circ$   
 $\mu = 3.12$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Irregular block, blue  
 0.30 × 0.28 × 0.25 mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\omega$  scans at fixed  $\chi = 55^\circ$   
 Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)  
 $T_{min} = 0.409$ ,  $T_{max} = 0.458$   
 4497 measured reflections

1107 independent reflections  
 949 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.032$   
 $\theta_{max} = 27.4^\circ$   
 $h = -13 \rightarrow 8$   
 $k = -12 \rightarrow 13$   
 $l = -10 \rightarrow 10$   
 Intensity decay: <1%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.097$   
 $S = 1.06$   
 1107 reflections  
 70 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 0.9805P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.97 e \text{ \AA}^{-3}$   
 $\Delta\rho_{min} = -0.77 e \text{ \AA}^{-3}$   
 Extinction correction: SHELXL97 (Sheldrick, 1997)  
 Extinction coefficient: 0.011 (2)

**Table 1**

Selected geometric parameters (Å, °) for (I).

Cu–N1	2.142 (3)		
N1–Cu–N1 <sup>i</sup>	90.11 (10)	N1–Cu–N1 <sup>iii</sup>	180.00 (11)
N1–Cu–N1 <sup>ii</sup>	89.89 (10)		

Symmetry codes: (i)  $x - y, x, -z$ ; (ii)  $-x + y, -x, z$ ; (iii)  $-x, -y, -z$ .

**Table 2**

Selected geometric parameters (Å, °) for (II).

Cu–N1	2.128 (2)		
N1–Cu–N1 <sup>i</sup>	180.0 (12)	N1–Cu–N1 <sup>iii</sup>	89.80 (7)
N1–Cu–N1 <sup>ii</sup>	90.20 (7)		

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $x - y, x, -z$ ; (iii)  $-x + y, -x, z$ .

## Compound (II)

### Crystal data

$[Cu(C_3H_4N_2)_6](PF_6)_{1.29}(ClO_4)_{0.71}$   
 $M_r = 729.90$   
 Trigonal,  $P\bar{3}$   
 $a = 9.995$  (1) Å  
 $b = 9.995$  (1) Å  
 $c = 8.052$  (1) Å  
 $V = 696.63$  (13) Å<sup>3</sup>  
 $Z = 1$   
 $D_x = 1.740$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 4084 reflections  
 $\theta = 1.0$ – $27.5^\circ$   
 $\mu = 1.03$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Irregular block, blue  
 0.4 × 0.4 × 0.4 mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\omega$  scans at fixed  $\chi = 55^\circ$   
 Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)  
 $T_{min} = 0.623$ ,  $T_{max} = 0.685$   
 4132 measured reflections

1072 independent reflections  
 967 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.030$   
 $\theta_{max} = 27.5^\circ$   
 $h = -12 \rightarrow 10$   
 $k = -12 \rightarrow 12$   
 $l = -10 \rightarrow 10$   
 Intensity decay: <1%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.096$   
 $S = 1.07$   
 1072 reflections  
 82 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0490P)^2 + 0.3481P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.002$   
 $\Delta\rho_{max} = 0.27 e \text{ \AA}^{-3}$   
 $\Delta\rho_{min} = -0.60 e \text{ \AA}^{-3}$

H atoms were found in difference Fourier maps and were refined using a riding model, with distances N–H = 0.88 Å and C–H = 0.95 Å. Upon refinement, the crystal of (II) was found to contain a mixture of anions, the major component being the expected  $PF_6^-$ , with a small fraction of  $ClO_4^-$ . A disorder model was constructed by including a fractional Cl atom constrained to the same coordinates and anisotropic displacement parameters as the P atom, and fractional O-atom positions obtained from a difference Fourier map.

For both compounds, data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO-SMN (Otwinowski & Minor, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s)

used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97* and local procedures.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1038). Services for accessing these data are described at the back of the journal.

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