metal-organic compounds

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

Tom Otieno,[a]***** **Jaime R. Blanton,**[a] **M. Jason Hatfield,**[a] **Sherry L. Asher**[a] **and Sean Parkin**[b]

[a]Department of Chemistry, Eastern Kentucky University, Richmond, KY 40475-3102, USA, and [b]Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA
Correspondence e-mail: tom.otieno@eku.edu

The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$, $NaAsF_6$ and excess pyrazole yields hexakis(pyrazole-κN^2)copper(II) bis(hexafluoroarsenate), $[Cu(C_3H_4N_2)_6](AsF_6)_2$ or $[Cu(pzH)_6](AsF_6)_2$ (pzH is pyrazole), (I). The analogous hexakis(pyrazole-κN^2)copper(II) hexafluorophosphate perchlorate complex, $[Cu(C_3H_4N_2)_6](PF_6)_{1.29}(ClO_4)_{0.71}$ or $[Cu(pzH)_6](PF_6)_{1.29}(ClO_4)_{0.71}$, (II), is obtained in a similar fashion, using KPF_6 in place of $NaAsF_6$. Both compounds contain the hitherto unknown $[Cu(pzH)_6]^{2+}$ 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 $[M(pzH)_n]X_p$, where M is a metal and X is an anion. Reported complexes with $n = 6$ include $[M(pzH)_6]X_2$, with $M = $ Mg, Mn, Fe, Co, Ni, Zn or Cd, and $X = NO_3$, BF_4 or ClO_4 (Trofimenko, 1972). The structures of $[Ni(pzH)_6](BF_4)_2$ (Ten-Hoedt et al., 1983), $[Ni(pzH)_6](NO_3)_2$ (Reimann et al., 1970) and $[Mn(pzH)_6](ClO_4)_2$ (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 Cu^{II} (Trofimenko, 1972; Nicholls & Warburton, 1971; Daugherty & Swisher, 1968). We attribute this lack of maximal coordination to the tendency of six-coordinate Cu^{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 Cu^{II} if non-coordinating anions were used and, therefore, undertook the

preparation of hexakis(pyrazole)copper(II) complexes using weakly ligating AsF_6^- and PF_6^- as the counter-ions. We have isolated two isostructural salts containing the $[Cu(pzH)_6]^{2+}$ complex cation, namely $[Cu(pzH)_6](AsF_6)_2$, (I), and $[Cu(pzH)_6](PF_6)_{1.29}(ClO_4)_{0.71}$, (II), and their crystal structures are presented here.

(I)

(II)
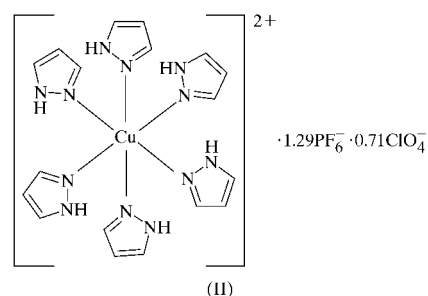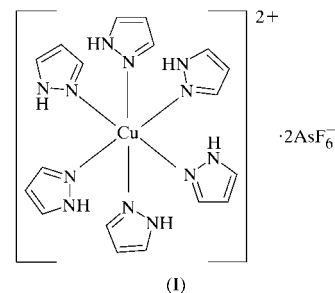
The Cu^{II} atoms in (I) (Fig. 1 and Table 1) and (II) (Fig. 2 and Table 2) occupy sites with $\bar{3}$ symmetry, requiring symmetry-equivalent Cu—N bonds. Such equal copper–ligand bond distances are atypical for Cu^{II} and warrant further discussion. Six-coordinate Cu^{II} complexes tend to have distorted 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 $[Cu(H_2O)_6](BrO_3)_2$ (Blackburn et al., 1991) and $[K_2Pb(Cu(NO_2)_6]$ (Isaacs & Kennard, 1967), which contain monodentate ligands, $[Cu(en)_3](SO_4)$ (en is ethylenediamine; Cullen & Lingafelter, 1970), which contains three bidentate ligands, and $[Cu(ompa)_2](ClO_4)_2$ (ompa is octamethylpyrophosphoramide; Joesten et al., 1968, 1970) and $[Cu(tach)_2](NO_3)_2$ (tach is cis,cis-1,3,5-triaminocylohexane; Ammeter et al., 1979), which contain two tridentate ligands.
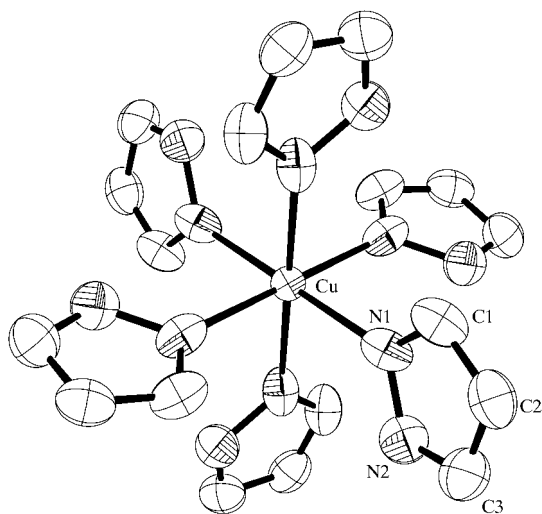
One explanation of these apparent violations of the Jahn–Teller theorem is the existence of a dynamic Jahn–Teller distortion, i.e. the complex could oscillate between three possible distortions, giving a regular time average. A second possibility is disordered static Jahn–Teller distortion, in which 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 &
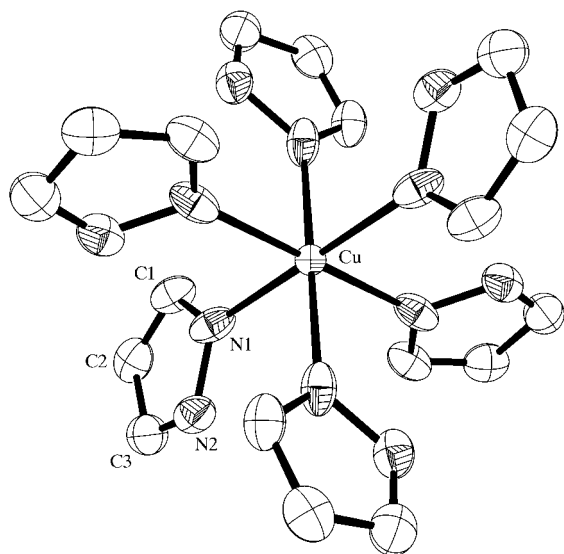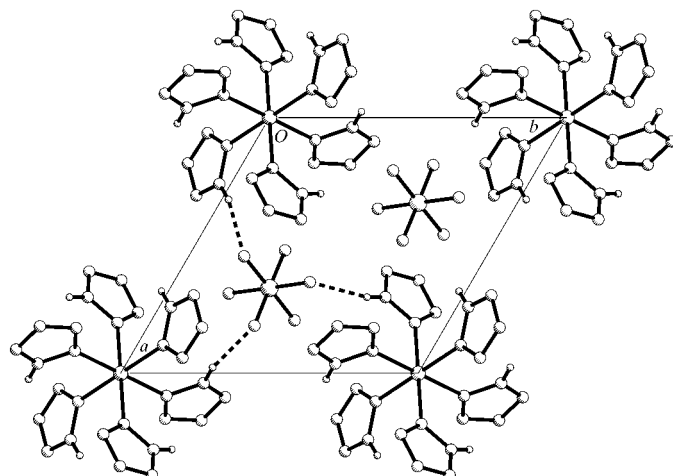
Figure 1
A view of the structure of the cation of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

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.

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° in (I) and 26.2° in (II). In contrast, a much larger angle (49.5°) is observed for the isomorphous Ni[II] complex, $[Ni(pzH)_6](NO_3)_2$, which is not subject to Jahn–Teller effects. These effects are also quantifiable in terms of ΔU values (Chandrasekhar & Bürgi, 1984). For compounds (I) and (II), the ΔU values along the Cu—N1 bonds are 0.0323 and 0.0324 Å^2, respectively. These are roughly an order of magnitude larger than the ΔU values for the other bonded pairs of atoms in the pyrazole ring in both (I) and (II). They

are also relatively larger than the value of 0.0105 Å^2 obtained for ΔU along the Ni—N1 bond in $[Ni(pzH)_6](NO_3)_2$.

Hydrogen bonds in (I) and (II) create an extended network of $[Cu(pzH)_6]^{2+}$ and AsF_6^- or 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 AsF_6^- ion [H2···F1 = 2.074 (3) Å]. Each AsF_6^- anion forms hydrogen bonds to three different $[Cu(pzH)_6]^{2+}$ moieties, and each $[Cu(pzH)_6]^{2+}$ moiety forms hydrogen bonds to six different 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[II] ion. The energy of the peak maximum in the visible spectra (15 100 cm^{-1}) is comparable with those observed for other complexes containing the $[CuN_6]^{2+}$ chromophore (McKenzie, 1970). The IR bands for the PF_6^- and AsF_6^- moieties are assigned on the basis of data from previously characterized hexafluorophosphate and hexafluoroarsenate complexes (Morrison & Thompson, 1982). For (I), ν_3 and ν_4 of the AsF_6^- group are observed at 705 and 411 cm^{-1}, respectively, and show no splitting. The corresponding bands for the PF_6^- group in (II) are observed at 840 and 561 cm^{-1}, respectively. These data are consistent with criteria for non-coordinating AsF_6^- or PF_6^- moieties (Morrison & Thompson, 1982).

Experimental

To prepare compound (I), a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.849 g, 2.29 mmol) in ethanol (5 ml) containing 10% *v/v* 2,2-dimethoxy-propane was added to $NaAsF_6$ (0.961 g, 4.54 mmol) dissolved in the same solvent (30 ml). The mixture was stirred for 15 min and filtered. To the filtrate was added more $NaAsF_6$ (0.500 g, 2.36 mmol), and the mixture was once again stirred for 15 min and then filtered into a solution of pyrazole (1.00 g, 14.7 mmol) in the above solvent (4 ml).

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.

metal-organic compounds

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 (λ_{max}, nm, MeOH): 664; ε ($dm^3\ mol^{-1}\ cm^{-1}$): 33; IR (ν, cm^{-1}, AsF_6^-): 705 ($v\ s$), 411 (s); μ_{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 (λ_{max}, nm, MeOH): 663; ε ($dm^3\ mol^{-1}\ cm^{-1}$): 34; IR (ν, cm^{-1}, PF_6^-): 840 ($v\ s$), 561 (s); μ_{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$_3$H$_4$N$_2$)$_6$](AsF$_6$)$_2$
$M_r = 849.87$
Trigonal, $P\overline{3}$
$a = 10.1780\ (14)$ Å
$b = 10.1780\ (14)$ Å
$c = 8.0980\ (16)$ Å
$V = 726.5\ (2)$ Å^3
$Z = 1$
$D_x = 1.943$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3793 reflections
$\theta = 1.0–27.5°$
$\mu = 3.12$ mm^{-1}
$T = 173\ (2)$ K
Irregular block, blue
$0.30 \times 0.28 \times 0.25$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans at fixed $\chi = 55°$
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 $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.4°$
$h = -13 \rightarrow 8$
$k = -12 \rightarrow 13$
$l = -10 \rightarrow 10$
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 Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.011 (2)

Table 1
Selected geometric parameters (Å, °) for (I).

Cu—N1	2.142 (3)		
N1—Cu—N1^i	90.11 (10)	N1—Cu—N1^{iii}	180.00 (11)
N1—Cu—N1^{ii}	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^i	180.0 (12)	N1—Cu—N1^{iii}	89.80 (7)
N1—Cu—N1^{ii}	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$_3$H$_4$N$_2$)$_6$](PF$_6$)$_{1.29}$(ClO$_4$)$_{0.71}$
$M_r = 729.90$
Trigonal, $P\overline{3}$
$a = 9.995\ (1)$ Å
$b = 9.995\ (1)$ Å
$c = 8.052\ (1)$ Å
$V = 696.63\ (13)$ Å^3
$Z = 1$
$D_x = 1.740$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4084 reflections
$\theta = 1.0–27.5°$
$\mu = 1.03$ mm^{-1}
$T = 173\ (2)$ K
Irregular block, blue
$0.4 \times 0.4 \times 0.4$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans at fixed $\chi = 55°$
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 $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -10 \rightarrow 10$
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 Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-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: *SHELXS*97 (Sheldrick, 1997); program(s)

used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97 and local procedures.

References

Ammeter, J. H., Bürgi, H. B., Gamp, E., Meyer-Sandrin, V. & Jensen, W. P. (1979). *Inorg. Chem.* **18**, 733–750.
Blackburn, A. C., Gallucci, J. C. & Gerkin, R. E. (1991). *Acta Cryst.* C**47**, 2019–2023.
Chandrasekhar, K. & Bürgi, H.-B. (1984). *Acta Cryst.* B**40**, 387–397.
Cullen, D. L. & Lingafelter, E. C. (1970). *Inorg. Chem.* **9**, 1858–1864.
Daugherty, N. A. & Swisher, J. H. (1968). *Inorg. Chem.* **7**, 1651–1653.
Ham, N. S. (1962). *Spectrochim. Acta*, **18**, 775–789.
Hathaway, B. J. & Billing, D. E. (1970). *Coord. Chem. Rev.* **5**, 143–207.
Isaacs, N. W. & Kennard, C. H. L. (1967). *J. Chem. Soc. Chem. Commun.* pp. 587–588.
Joesten, M. D., Hussain, M. S. & Lenhert, P. G. (1970). *Inorg. Chem.* **9**, 151–162.
Joesten, M. D., Hussain, M. S., Lenhert, P. G. & Venable, J. H. Jr (1968). *J. Am. Chem. Soc.* **90**, 5623–5625.
Lumme, P. O., Lindell, E. & Mutikainen, I. (1988). *Acta Cryst.* C**44**, 967–970.
McKenzie, E. D. (1970). *J. Chem. Soc. A*, pp. 3095–3099.
Morrison, R. M. & Thompson, R. C. (1982). *Can. J. Chem.* **60**, 1048–1054.
Nicholls, D. & Warburton, B. A. (1971). *J. Inorg. Nucl. Chem.* **33**, 1041–1045.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
Reimann, C. W., Santoro, A. & Mighell, A. D. (1970). *Acta Cryst.* B**26**, 521–526.
Sheldrick, G. M. (1994). *SHELXTL.* Release 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Steel, P. J. (1990). *Coord. Chem. Rev.* **106**, 227–265.
Ten-Hoedt, R. W. M., Driessen, W. L. & Verschoor, G. C. (1983). *Acta Cryst.* C**39**, 71–72.
Trofimenko, S. (1986). *Prog. Inorg. Chem.* **34**, 115–210.
Trofimenko, S. (1972). *Chem. Rev.* **72**, 497–509.