Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis[bis(3-phenylpyrazol-1-yl)(pyrazol-1-yl)methane]copper(II) bis(perchlorate) acetonitrile disolvate

M. Scott Goodman,[a] Margaret A. Goodman,[a] Andrey Y. Kovalevsky,[b] Alexander Y. Nazarenko[a]* and Donald Pope[a]

[a]Chemistry Department, State University of New York, College at Buffalo, 1300 Elmwood Ave, Buffalo, NY 14222-1095, USA, and [b]Department of Chemistry, State University of New York, University at Buffalo, Buffalo, NY 14260, USA
Correspondence e-mail: nazareay@buffalostate.edu

Received 16 November 2005
Accepted 13 December 2005
Online 14 January 2006

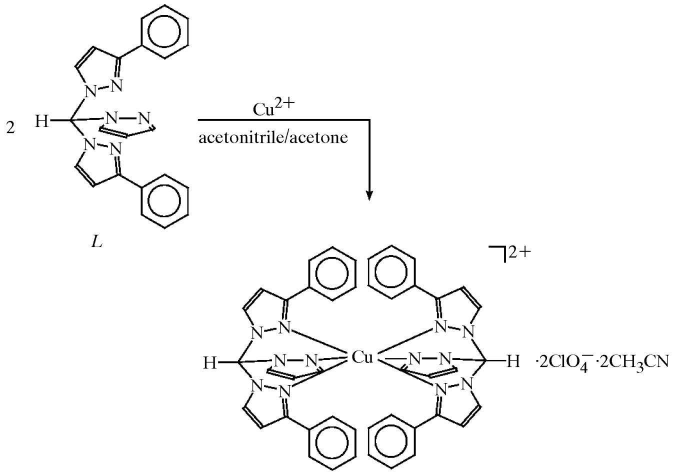
The title copper(II) complex, $[Cu(C_{22}H_{18}N_6)_2](ClO_4)_2\cdot 2C_2H_3N$, comprises two neutral substituted tris(pyrazol-1-yl)methane ligands bonded to a central Cu^{II} ion, which is positioned on a crystallographic inversion center. Six Cu—N bonds are arranged in a distorted octahedral fashion. The unsubstituted pyrazole rings on each ligand are oriented *trans* with respect to each other, interdigitated with the two 3-phenylpyrazole rings of the other ligand.

Comment

The transition metal complexes of tris(pyrazolyl)methanes (Tpms) have been known for over 30 years (Trofimenko, 1970; Reger, 1999). Several structural studies on 2:1 Tpm–copper(II) complexes have been undertaken. These include the Cu^{II} complexes with tris(3,5-dimethylpyrazolyl)methane (Reger *et al.*, 2002; Martini *et al.*, 2002), tris(3,4,5-trimethylpyrazolyl)methane (Martini *et al.*, 2002), tris(4-bromo-3,5-dimethylpyrazolyl)methane (Cvetkovic *et al.*, 2001) and tris(pyrazolyl)methane (Astley *et al.*, 1993). With Cu^{II}, these tripodal *N*-donor ligands typically form 2:1 octahedral complexes, showing Jahn–Teller distortion typical of d^9 metal complexes. Other stoichiometries are also possible (Cvetkovic *et al.*, 2001; Moubaraki *et al.*, 2002; Van Langenberg *et al.*, 2002).

A common feature of all the tris(pyrazolyl)methane ligands studied thus far is that they each have C_{3v} symmetry, *viz*. they are all constructed using three identical pyrazole moieties. In this report, for the first time, we present the structure of a metal complex that incorporates a tris(pyrazolyl)methane ligand constructed from two different pyrazoles (see scheme). Ligand *L*, namely bis(3-phenylpyrazolyl)(pyrazolyl)methane, incorporates two 3-phenylpyrazole moieties and a single unsubstituted pyrazole ring. Upon mixing with 0.5 equivalents of copper(II) perchlorate in acetonitrile/acetone, the green complex $[CuL_2](ClO_4)_2\cdot 2C_2H_3N$, (I) (Fig. 1), crystallizes.

There are two possible isomers of the complex, which differ in the position of the unsubstituted pyrazole moieties relative to each other in the complex. A centrosymmetric complex with two unsubstituted pyrazole moieties opposite each other clearly has less steric hindrance than an asymmetric isomer with juxtaposed unsubstituted groups.



(I)

Previously reported structures of symmetric tris(pyrazolyl)methane–copper(II) complexes demonstrate a typically Jahn–Teller-distorted geometry, with two short C—N distances of approximately 2.0 Å and one long distance of 2.35 Å. In the title compound, the additional effect of the unsubstituted pyrazole group results in further variety of the bond distances (Table 1), one becoming significantly shorter [1.9433 (13) Å]

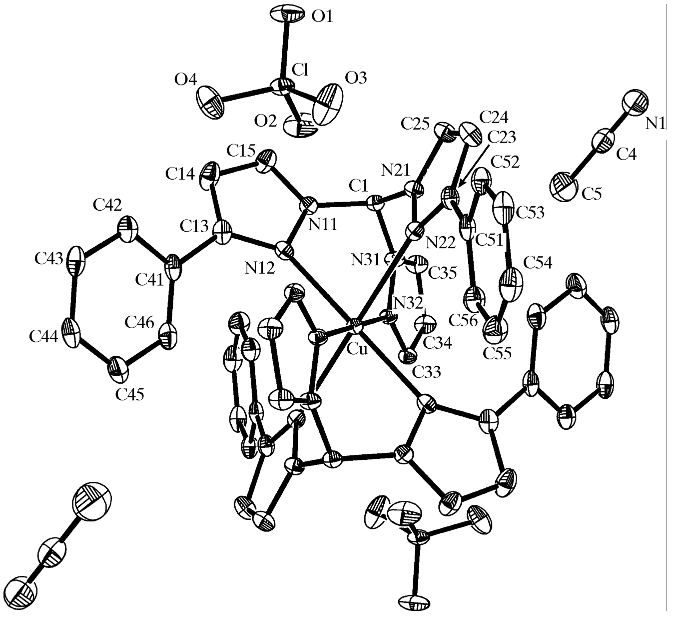


Figure 1
A view of the molecule of $[CuL_2](ClO_4)_2\cdot 2C_2H_3N$, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

DOI: 10.1107/S0108270105041661

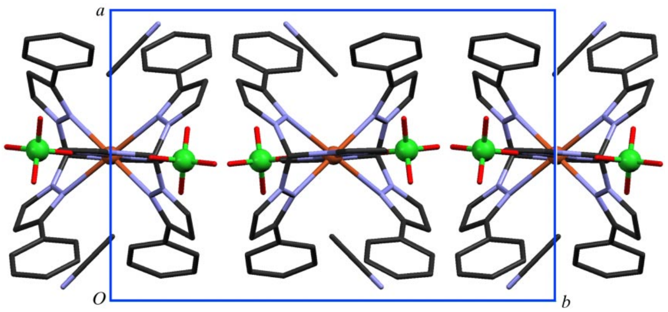


Figure 2
The packing of $[CuL_2](ClO_4)_2\cdot 2C_2H_3N$, viewed along the *c* axis.

and another much longer [2.1878 (14) Å]. The bite angles between unsubstituted pyrazole atom N32 and phenylpyrazole atoms N12 and N22 are only slightly smaller than 90° (Table 1), while the angle between the two phenylpyrazole N atoms is visibly less [79.19 (5)°]. Once again, it appears that steric hindrance is playing a dominant role.

The central Cu^{II} atom along with axial atom C1 and each corresponding pair of pyrazole groups form three planes. In agreement with planarity of the copper–pyrazole complex, the torsion angles around the N—N bond are small, being almost zero for the unsubstituted pyrazole moiety (Table 1). The mean deviation of atoms from the plane containing the unsubstituted pyrazole ring is less than 0.01 Å, while for the other two planes these deviations are visibly larger (0.04 Å). These three planes intercept each other very close to the C1—Cu axis, thus forming the main motif of a complex cation. The same shape of the complex can be achieved *via* molecular simulations using semi-empirical calculations in the PM3 approximation. The angles between the planes are 73.5, 53.0 and 53.5°, with the largest corresponding to that between the two substituted pyrazole groups.

The cationic complexes are positioned with the copper ion on a crystallographic inversion center. The metal ion is surrounded by a hydrophobic 'coat', thus leaving no possibility for any additional interactions. The perchlorate ions and solvent molecules fill voids in the crystal structure, which shows no hydrogen bonds or short contacts (Fig. 2).

Experimental

Ligand *L* was prepared using a method similar to that previously described by Goodman & Bateman (2001). Tris(pyrazolyl)methane (2.00 g, 9.3 mmol) and 3-phenylpyrazole (4.00 g, 27.7 mmol) were dissolved in dry toluene (250 ml) in a 500 ml round-bottomed flask. *p*-Toluenesulfonic acid (1.60 g, 9.3 mmol) was added and the reaction mixture refluxed for 24 h under argon. The cooled reaction mixture was poured into saturated aqueous $NaHCO_3$ (150 ml), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 ml) and the combined organic layers were washed with water (100 ml). The organic extracts were dried with Na_2SO_4 and evaporated, affording a mixture consisting of all possible substitution products, 3-phenylpyrazole and pyrazole. The crude product was dissolved in a small amount of dichloromethane and applied to a silica column. The column was first eluted with a 4:1 dichloromethane/ethyl acetate mixture. The polarity was slowly increased to 3:1 dichloromethane/ethyl acetate. The order of elution is based on the number of 3-phenylpyrazoles incorporated into the Tpm. Trisubstituted tris(3-phenylpyrazolyl)methane elutes first, followed by disubstituted *L* and, finally, monosubstituted (3-phenylpyrazolyl)bis(pyrazolyl)methane. Ligand *L*: ^{1}H NMR: δ 6.37 (*t*, *J* = 4.3 Hz, 1H), 6.67 (*d*, *J* = 2.6 Hz, 2H), 7.32 (*t*, *J* = 7.1 Hz, 2H), 7.39 (*t*, *J* = 6.6 Hz, 4H), 7.66 (*d*, *J* = 2.6 Hz, 3H), 7.68 (*d*, *J* = 1.3 Hz, 1H), 7.81 (*d*, *J* = 6.9 Hz, 4H), 8.48 (*s*, 1H); ^{13}C NMR: δ 83.7, 104.6, 107.2, 126.0, 128.4, 128.6, 129.6, 130.8, 132.5, 141.8, 153.6; EIMS *m*/*z*: 366 (M^+), 223. EI–HRMS: calculated for $C_{22}H_{18}N_6$: 366.1593; found: 366.1590. For the preparation of the Cu^{II} complex, a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (37 mg, 0.10 mmol) in acetonitrile (10 ml) was mixed with *L* (73 mg, 0.20 mmol) dissolved in acetone (10 ml). Upon standing, dark-green crystals suitable for X-ray diffraction were deposited on the sides of the tube.

Crystal data

$[Cu(C_{22}H_{18}N_6)_2](ClO_4)_2\cdot 2C_2H_3N$
$M_r = 1077.40$
Monoclinic, $P2_1/c$
$a = 11.3652$ (2) Å
$b = 16.3372$ (3) Å
$c = 14.0065$ (3) Å
$\beta = 109.949$ (1)°
$V = 2444.62$ (8) Å^3
$Z = 2$

$D_x = 1.464$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20256 reflections
$\theta = 3$–29°
$\mu = 0.63$ mm^{-1}
$T = 90$ (2) K
Prism, green
0.40 × 0.25 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.79$, $T_{max} = 0.88$
34957 measured reflections

5606 independent reflections
4998 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -21 \rightarrow 21$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.05$
5606 reflections
352 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 2.3608P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0099 (5)

Table 1
Selected geometric parameters (Å, °).

Cu—N32	1.9433 (13)	N21—C25	1.356 (2)
Cu—N12	2.1878 (14)	N21—N22	1.3635 (18)
Cu—N22	2.3500 (14)	N22—C23	1.339 (2)
C1—N21	1.441 (2)	C23—C24	1.408 (2)
C1—N31	1.4432 (19)	C24—C25	1.365 (2)
C1—N11	1.445 (2)	N31—C35	1.351 (2)
N11—C15	1.347 (2)	N31—N32	1.3543 (18)
N11—N12	1.3689 (18)	N32—C33	1.330 (2)
N12—C13	1.340 (2)	C33—C34	1.394 (2)
C13—C14	1.403 (3)	C34—C35	1.369 (2)
C14—C15	1.367 (3)		
N32—Cu—N12	88.60 (5)	N32^i—Cu—N22	92.39 (5)
N32^i—Cu—N12	91.40 (5)	N12—Cu—N22	79.19 (5)
N32—Cu—N22	87.61 (5)	N12^i—Cu—N22	100.81 (5)
C1—N11—N12—Cu	−10.75 (17)	C1—N31—N32—Cu	−2.43 (19)
C1—N21—N22—Cu	6.78 (16)		

Symmetry code: (i) $-x+1, -y, -z+1$.

All H atoms were located in a difference map and then allowed to ride on their parent C atoms, with U_{iso}(H) values of $1.2U_{eq}$(C) for aromatic and $1.5U_{eq}$(C) for methyl H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

X-ray data were collected at the University of Buffalo. The authors thank Dr Philip Coppens (UB) for his helpful guidance and kind permission to use the diffractometer. Financial support from the ACS PRF fund is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1025). Services for accessing these data are described at the back of the journal.

References

Astley, T., Gulbis, J. M., Hitchman, M. A. & Tiekink, E. R. T. (1993). *J. Chem. Soc. Dalton Trans.* pp. 509–515.

Bruker (1998). *SMART* and *SAINT*. Versions 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Cvetkovic, M., Batten, S. R., Moubaraki, B., Murray, K. S. & Spiccia, L. (2001). *Inorg. Chim. Acta*, **324**, 131–140.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Goodman, M. S. & Bateman, M. A. (2001). *Tetrahedron Lett.* **42**, 5–7.

Martini, D., Pellei, M., Pettinari, C., Skelton, B. W. & White, A. H. (2002). *Inorg. Chim. Acta*, **333**, 72–82.

Moubaraki, B., Murray, K. S. & Tiekink, E. R. T. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 219–220.

Reger, D. L. (1999). *Comments Inorg. Chem.* **21**, 1–28.

Reger, D. L., Little, C. A., Smith, M. D. & Long, G. J. (2002). *Inorg. Chem.* **41**, 4453–4460.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Trofimenko, S. (1970). *J. Am. Chem. Soc.* **92**, 5118–5126.

Van Langenberg, K. A., Moubaraki, B., Murray, K. S. & Tiekink, E. R. T. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 223–224.