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Key indicators

Single-crystal X-ray study
 T = 173 K
 Mean $\sigma(C-C)$ = 0.012 Å
 R factor = 0.055
 wR factor = 0.131
 Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

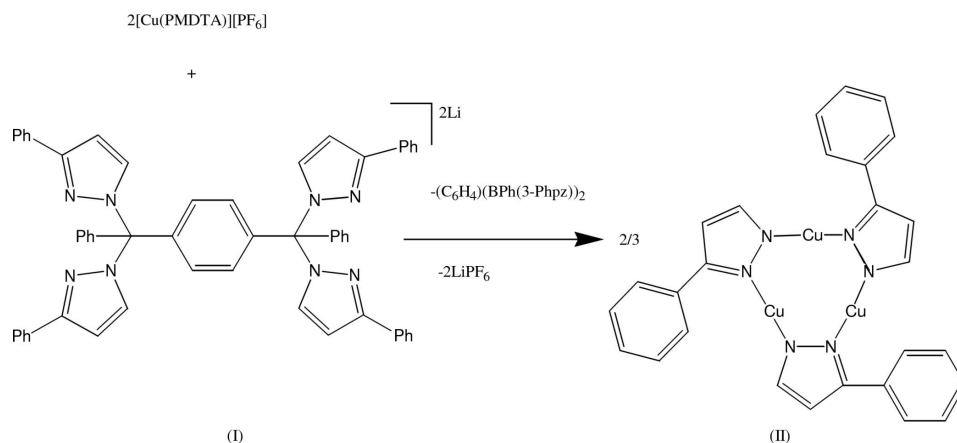
cyclo-Tris(μ_2 -3-phenyl-1H-pyrazole)tricopper(I)

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The crystal structure of the title compound, $[Cu_3(C_9H_7N_2)_3]$, consists of discrete Cu^I -phenylpyrazolyl trimers, with Cu atoms bridged by *exo*-bidentate phenylpyrazolyl ligands having short intramolecular $Cu \cdots Cu$ contacts [3.2076 (14)–3.2402 (14) Å]. The Cu_3N_6 nine-membered rings are essentially planar.

Comment

Following the first synthesis of a scorpinate complex, considerable progress has been made towards extending this area of chemistry (Trofimenko, 1993). Our studies have shown that an important factor influencing the stability of scorpinates appears to be the degree of steric crowding around the boron centre. The investigations in our group show that the scorpinates $RB(3-R'pz)_3^-$ and $RB(4-R'pz)_3^-$ decompose in the presence of transition metal salts much more easily when *R* and *R'* are bulky (Bieller *et al.*, 2006). We now have found that treatment of ditopic dilithium scorpinate, (I), with $[Cu(PMDTA)][PF_6]$ (PMDTA = pentamethyldiethylenetriamine) leads also to the formation of tris(μ_2 -3-phenylpyrazole)tricopper(I), (II).



The crystal structure of the title complex contains neutral trimeric copper(I)phenylpyrazolyl molecules with approximate C_3 molecular symmetry. The molecular structure is depicted in Fig. 1 together with the labeling scheme. The title complex, like many other homoleptic pyrazolates of group 11 metals (*e.g.* Ardizzioia *et al.*, 1998; Raptis & Fackler, 1988; Ehlert *et al.*, 1992), exhibits a triangular arrangement of metal atoms with all edges bridged by *exo*-bidentate phenylpyrazole ligands with distances of 3.2076 (14), 3.2083 (15) and 3.2402 (14) Å for $Cu1 \cdots Cu3$, $Cu2 \cdots Cu3$ and $Cu1 \cdots Cu2$, respectively. The Cu atoms are linearly coordinated by two N

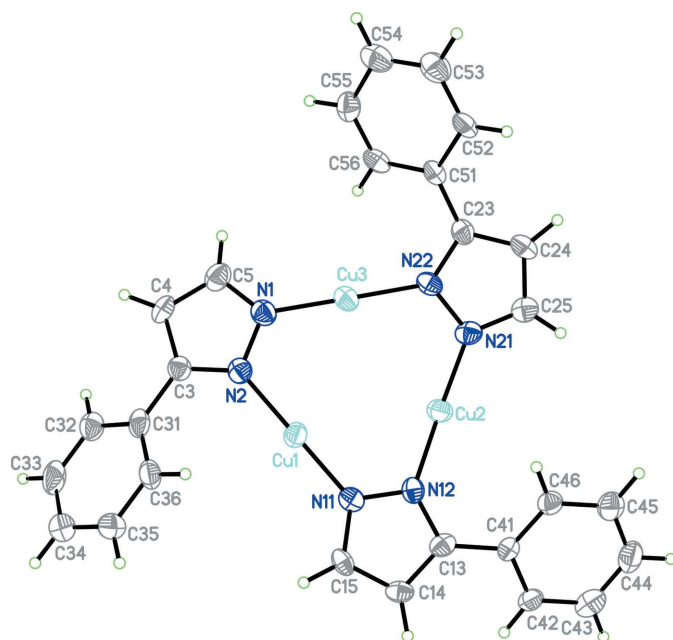


Figure 1
Perspective view of the title compound, with the atom-numbering scheme; displacement ellipsoids are at the 50% probability level; H atoms are drawn as small spheres of arbitrary radii.

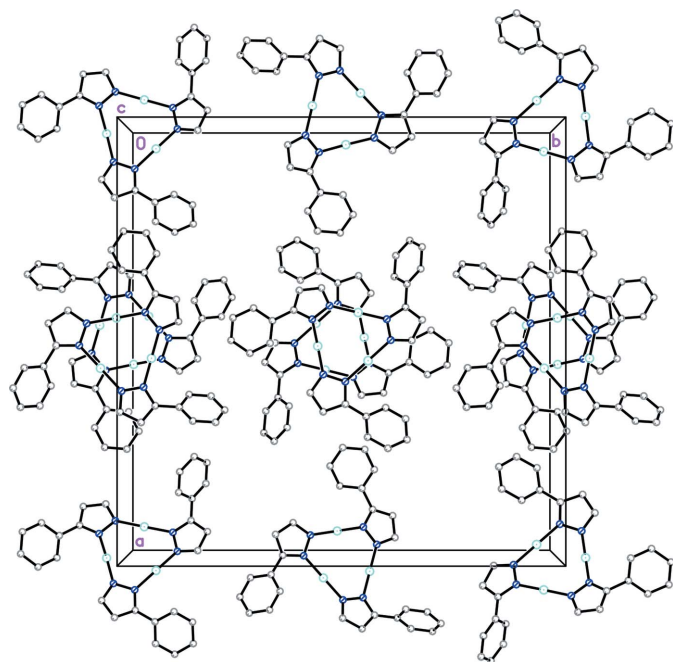


Figure 2
Packing diagram of the title compound, with view along the *c* axis. H atoms have been omitted.

atoms of phenylpyrazolyl ligands (Table 1), which lie in the plane of the metal atoms (r.m.s. deviation for all Cu and N atoms = 0.084 Å). The phenyl rings are twisted out of the plane of the pyrazolyl rings to which they are attached by 30.8 (4), 32.5 (3) and 37.4 (3)° for N1–C5, N11–C15 and N21–C25, respectively. In the crystal structure, molecules are stacked along the *c* axis (Fig. 2).

Experimental

A solution of (I) (0.036 g, 0.042 mmol) in tetrahydrofuran (10 ml) was treated with [Cu(PMDTA)][PF₆] (0.084 mmol). Colourless crystals of (II) suitable for X-ray diffraction were grown by slow diffusion of hexane into this solution at room temperature.

Crystal data

[Cu₃(C₉H₇N₂)₃]
M_r = 620.12
 Tetragonal, *P4/n*
a = 26.6249 (19) Å
c = 7.1739 (7) Å
V = 5085.5 (7) Å³
Z = 8

D_x = 1.620 Mg m⁻³
 Mo *K*α radiation
 μ = 2.51 mm⁻¹
T = 173 (2) K
 Needle, colourless
 0.19 × 0.09 × 0.08 mm

Data collection

Stoe IPDS-II two-circle diffractometer
 ω scans
 Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.647, *T_{max}* = 0.824

29854 measured reflections
 4701 independent reflections
 2005 reflections with *I* > 2σ(*I*)
R_{int} = 0.090
 θ_{\max} = 25.5°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.055
wR(*F*²) = 0.131
S = 0.79
 4701 reflections
 325 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0458P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.93 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.66 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1–N11	1.852 (7)	Cu2–N12	1.867 (7)
Cu1–N2	1.857 (7)	Cu3–N1	1.849 (7)
Cu2–N21	1.845 (7)	Cu3–N22	1.864 (7)
<hr/>			
N11–Cu1–N2	177.8 (3)	N1–Cu3–N22	178.5 (3)
N21–Cu2–N12	173.6 (3)		

H atoms were located in a difference map, but were refined with fixed individual displacement parameters [*U*_{iso}(H) = 1.2*U*_{eq}(C)] using a riding model with C–H = 0.95 Å. The highest peak is located at *x* = 0.736, *y* = 0.708, *z* = 0.431, which is located 3.11 Å from H42. *PLATON* (Spek, 2003) detected a solvent accessible void of approximately 141 Å³ including the position of this peak. It could be argued that this void could have initially contained tetrahydrofuran or hexane solvent molecules but these molecules have since evaporated from the structure without degradation of the crystal.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

References

Ardisioia, G. A., Cenini, S., La Monica, G., Masciocchi, N., Maspero, A. & Moret, M. (1998). *Inorg. Chem.* **37**, 4284–4292.

- Bieller, S., Haghiri, A., Bolte, M., Bats, J. W., Wagner, M. & Lerner, H.-W. (2006). *Inorg. Chim. Acta*, **359**, 1559–1572.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Ehlert, M. K., Rettig, S. J., Storr, A., Thompson, R. C. & Trotter, J. (1992). *Can. J. Chem.* **70**, 2161–2173.
- Raptis, R. G. & Fackler, J. P. Jr (1988). *Inorg. Chem.* **27**, 4179–4182.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **A36**, 7–13.
- Stoe & Cie (2001). *X-Area*. Stoe & Cie, Darmstadt, Germany.
- Trofimenko, S. (1993). *Chem. Rev.* **93**, 943–980.