

In situ synthesis of mononuclear copper(II) complexes of the new tridentate ligand bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine

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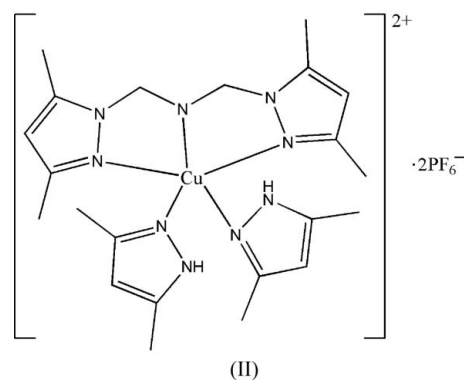
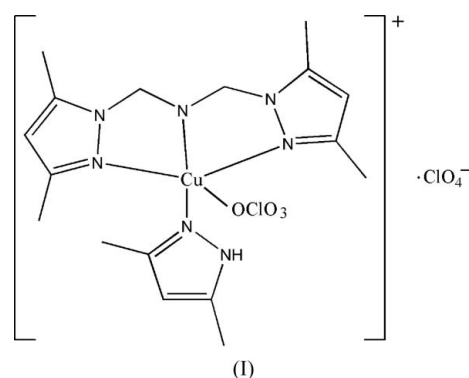
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Two mononuclear copper complexes, $\{\text{bis}[(3,5\text{-dimethyl-1}H\text{-pyrazol-1-yl-}\kappa N^2)\text{methyl}] \text{amine-}\kappa N\}(3,5\text{-dimethyl-1}H\text{-pyrazole-}\kappa N^2)(\text{perchlorato-}\kappa O)\text{copper(II) perchlorate}$, $[\text{Cu}(\text{ClO}_4)(\text{C}_5\text{H}_8\text{N}_2)(\text{C}_{12}\text{H}_{19}\text{N}_5)]\text{ClO}_4$, (I), and $\{\text{bis}[(3,5\text{-dimethyl-1}H\text{-pyrazol-1-yl-}\kappa N^2)\text{methyl}] \text{amine-}\kappa N\}\text{bis}(3,5\text{-dimethyl-1}H\text{-pyrazole-}\kappa N^2)\text{copper(II) bis(hexafluoridophosphate)}$, $[\text{Cu}(\text{C}_5\text{H}_8\text{N}_2)_2(\text{C}_{12}\text{H}_{19}\text{N}_5)](\text{PF}_6)_2$, (II), have been synthesized by the reactions of different copper salts with the tripodal ligand tris[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine (TDPA) in acetone–water solutions at room temperature. Single-crystal X-ray diffraction analysis revealed that they contain the new tridentate ligand bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine (BDPA), which cannot be obtained by normal organic reactions and has thus been captured in the solid state by *in situ* synthesis. The coordination of the Cu^{II} ion is distorted square pyramidal in (I) and distorted trigonal bipyramidal in (II). The new *in situ* generated tridentate BDPA ligand can act as a meridional or facial ligand during the process of coordination. The crystal structures of these two compounds are stabilized by classical hydrogen bonding as well as intricate nonclassical hydrogen-bond interactions.

Comment

Polydentate pyrazole ligands, which can act as terminal chelate ligands coordinated to metal ions, have been shown to be efficient in the construction of metalloenzymes (Melnik, 1982). These compounds, built of copper ions and polydentate pyrazole ligands, can also be regarded as models for bioinorganic systems, as well as for the discovery of new catalyst precursors. In order to expand the range of metalloenzymes and to obtain a deeper insight into the biologically interesting effects of complexes of polydentate pyrazole ligands with metal ions, it is important to design and synthesize new terminal polydentate ligands for the construction of metalloenzymes. *In situ* metal–ligand reactions, which have been

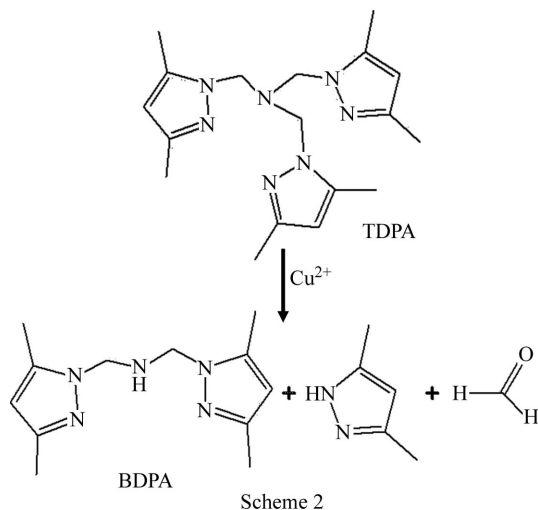
investigated for many decades, are a very important method for the generation of novel coordination compounds with ligands that are inaccessible in normal organic reactions (Chen & Tong, 2007). To date, many kinds of functional compounds built out of *in situ* generated ligands and metal ions have been documented (Chen & Tong, 2007). Recently, our attempts to synthesize new types of mononuclear precursor compounds by the reaction of the Cu^{II} ion and the tripodal ligand tris[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine (TDPA) yielded two mononuclear Cu^{II} compounds with a new *in situ* generated tridentate ligand, bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]amine (BDPA). To the best of our knowledge, a successful synthetic route to the tridentate BDPA ligand has not yet been documented and synthetic attempts to obtain BDPA have failed due to the uncontrollable reaction of (pyrazol-1-yl)methanol and primary amines (Daoudi *et al.*, 2006). Here, with the help of *in situ* synthesis, the BDPA ligand has been captured in the solid state and characterized by single-crystal X-ray crystallography. The crystal structures of these mononuclear copper compounds, namely $\{\text{bis}[(3,5\text{-dimethyl-1}H\text{-pyrazol-1-yl-})\text{methyl}] \text{amine}\}(3,5\text{-dimethyl-1}H\text{-pyrazole-})(\text{perchlorato})\text{copper(II) perchlorate}$, (I), and $\{\text{bis}[(3,5\text{-dimethyl-1}H\text{-pyrazol-1-yl-})\text{methyl}] \text{amine}\}\text{bis}(3,5\text{-dimethyl-1}H\text{-pyrazole-})\text{copper(II) bis(hexafluoridophosphate)}$, (II), the characteristics of the new BDPA ligand and the possible mechanism of the *in situ* reaction are described herein.



Scheme 1

In the process of the coordination reaction between Cu^{II} salts and the tripodal TDPA ligand in a molar ratio of 1:1 in the open air, the tripodal ligand decomposes to the tridentate BDPA ligand (L1), 3,5-dimethyl-1*H*-pyrazole (L2) and

HCHO, as a result of C–N bond cleavage catalysed by the Cu^{II} ions in the reaction solution (see Scheme 2; Barszcz *et al.*, 2004). The new BDPA ligand is then stabilized *via* coordination with the Cu^{II} ion and is captured in the solid state. Thus, the new tridentate BDPA ligand, which cannot be obtained by normal organic synthesis, has been generated *in situ*.



A perspective view of the asymmetric unit of complex (I) is depicted in Fig. 1. The complex contains two different coordinated ligands obtained during the reaction process, *viz.* BDPA and *L2*, without the original tripodal TDPA ligand. The central Cu^{II} ion is five-coordinated by one tridentate chelate ligand (atoms N4, N6 and N7), one neutral pyrazole ligand (N2) and one coordinated perchlorate anion (O4). The coordination geometry around the Cu^{II} ion is presented in Table 1. The bond angles indicate that the coordination geometry can be best described as distorted square pyramidal. The equa-

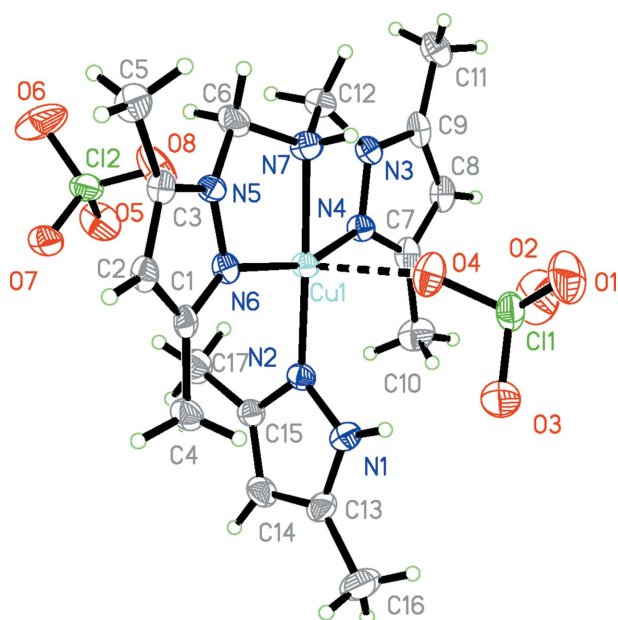


Figure 1
The asymmetric unit of (I), showing the atomic-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

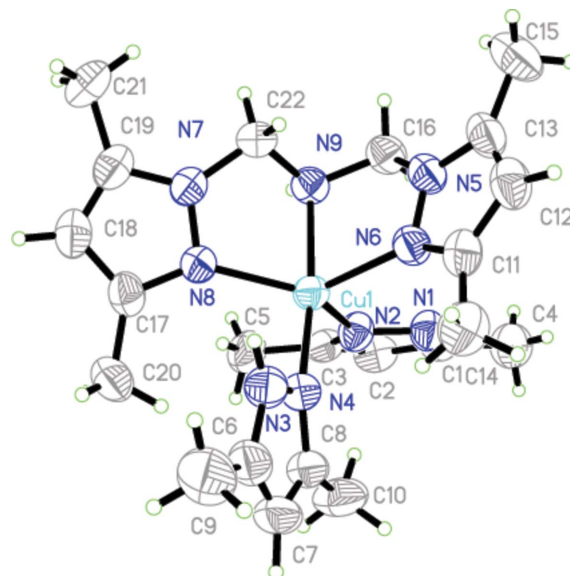


Figure 2
The asymmetric unit of (II), showing the atomic-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The hexafluoridophosphate counter-ions have been omitted for clarity.

torial sites are occupied by the three N atoms from *L1* and one N atom from *L2*, while the apical position is occupied by an O atom from one of the two independent perchlorate anions. The other perchlorate anion is noncoordinating. The tridentate BDPA ligand acts as a meridional ligand, with a dihedral angle between the two BDPA pyrazole rings of $12.39(3)^\circ$. The *in situ*-generated *L2* ligand coordinates to the central Cu^{II} ion *trans* to the central N atom (N7) of the BDPA ligand. The Cu–N bond lengths in (I) are similar to those observed for related Cu^{II} complexes with pyrazole and pyridine donor ligands (Watson *et al.*, 1987). There is an intramolecular hydrogen bond between the noncoordinating amine group of *L2* and an O atom of the coordinated perchlorate anion. The central amine group of the BDPA ligand also forms a hydrogen bond with the free perchlorate anion (Table 2), forming a hydrogen-bonded ion pair, but there is no extension of the classical hydrogen-bonding network beyond this. Two weak C–H...O interactions may be present (Table 2). One, involving C12–H12B is just a further interaction between the cation and free perchlorate anion involved in the described ion pair, while that involving C8–H8A links complex cations through the coordinated perchlorate ligand into extended chains which run parallel to the [010] direction.

In contrast with the crystal structure of (I), the central Cu^{II} ion in (II) is coordinated by five N atoms, three from the tridentate *L1* ligand (N6, N8 and N9) and the others from two independent *L2* ligands (N2 and N4) (Fig. 2). The tridentate *L1* ligand coordinates in a facial mode, with a dihedral angle between the two BDPA pyrazole rings of $58.95(2)^\circ$. The coordination geometry around the Cu^{II} ion is presented in Table 3, which indicates that the Cu^{II} ion has a slightly distorted trigonal bipyramidal geometry. The three equatorial positions are occupied by atoms N6, N8 and N2, and the axial positions are occupied by atoms N4 and N9. The two inde-

pendent hexafluoridophosphate anions occupy approximate columns between the cations. Several weak N—H...F interactions involving all N—H donors of the *L1* and *L2* ligands serve to link the ions into extended chains which run parallel to the [010] direction (Table 4). N3—H of one *L2* ligand has a bifurcated interaction with two F atoms of the same anion, while N9—H of the other *L2* ligand also has bifurcated interactions with two F atoms of the other independent cation. This latter anion also accepts the N1—H interaction and a very weak C4—H interaction from the central amine group of the BDPA ligand of a different cation, thereby forming the link that leads to the extended chain.

Experimental

An acetone solution (5 ml) of the tripodal ligand TDPA (0.1 mmol) was added to aqueous solutions (10 ml) of different copper salts [0.1 mmol Cu(ClO₄)₂ for (I) and (II)] and, after stirring the mixture at room temperature for 30 min, the counter-ions were added [0.5 mmol NaClO₄ for (I) and 0.5 mmol KPF₆ for (II)]. The resulting solutions were filtered and allowed to stand at room temperature, and two similar mononuclear single-crystal samples were obtained after one week (yields 40–45%).

Compound (I)

Crystal data

[Cu(ClO ₄)(C ₅ H ₈ N ₂)(C ₁₂ H ₁₉ N ₅)]-ClO ₄	$\beta = 105.938 (8)^\circ$
$M_r = 591.91$	$V = 4853.0 (5) \text{ \AA}^3$
Monoclinic, <i>C2/c</i>	$Z = 8$
$a = 37.574 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.5769 (4) \text{ \AA}$	$\mu = 1.18 \text{ mm}^{-1}$
$c = 15.661 (1) \text{ \AA}$	$T = 293 \text{ K}$
	$0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Oxford Gemini S Ultra diffractometer	11887 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	4701 independent reflections
$T_{\min} = 0.719$, $T_{\max} = 0.799$	2699 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	322 parameters
$wR(F^2) = 0.088$	H-atom parameters constrained
$S = 0.88$	$\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$
4701 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

Cu1—N2	1.941 (4)	Cl2—O8	1.415 (3)
Cu1—N4	1.991 (3)	Cl2—O7	1.423 (3)
Cu1—N6	2.001 (3)	Cl2—O6	1.423 (4)
Cu1—N7	2.023 (4)	Cl2—O5	1.448 (3)
Cu1—O4	2.373 (3)		
N2—Cu1—N4	98.76 (14)	N6—Cu1—N7	81.75 (14)
N2—Cu1—N6	97.31 (14)	N2—Cu1—O4	95.03 (13)
N4—Cu1—N6	160.43 (14)	N4—Cu1—O4	92.21 (11)
N2—Cu1—N7	178.50 (14)	N6—Cu1—O4	97.44 (11)
N4—Cu1—N7	81.93 (14)	N7—Cu1—O4	86.27 (13)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O3	0.86	2.05	2.876 (5)	161
N7—H7A...O5 ⁱ	0.91	2.21	3.029 (5)	149
C8—H8A...O3 ⁱⁱ	0.93	2.53	3.350 (5)	148
C12—H12B...O7 ⁱ	0.97	2.45	3.198 (5)	133

Symmetry codes: (i) $x, -y + 1, z + \frac{1}{2}$; (ii) $x, y - 1, z$.

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

Cu1—N4	1.987 (3)	Cu1—N2	2.089 (3)
Cu1—N8	2.034 (2)	Cu1—N6	2.100 (3)
Cu1—N9	2.068 (2)		
N4—Cu1—N8	92.93 (10)	N9—Cu1—N2	89.90 (10)
N4—Cu1—N9	168.90 (10)	N4—Cu1—N6	99.73 (11)
N8—Cu1—N9	79.36 (10)	N8—Cu1—N6	129.31 (10)
N4—Cu1—N2	101.10 (11)	N9—Cu1—N6	79.51 (10)
N8—Cu1—N2	125.04 (11)	N2—Cu1—N6	100.37 (10)

Table 4

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H3A...F8	0.86	2.32	3.136 (5)	158
N3—H3A...F7	0.86	2.34	3.101 (6)	148
N9—H9D...F3 ⁱ	0.91	2.32	3.088 (5)	142
N9—H9D...F1 ⁱ	0.91	2.39	3.069 (5)	131
N1—H1A...F2 ⁱⁱ	0.86	2.36	3.099 (5)	144
C4—H4A...F9 ⁱⁱ	0.96	2.47	3.333 (8)	149

Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

Compound (II)

Crystal data

[Cu(C ₅ H ₈ N ₂)(C ₁₂ H ₁₉ N ₅)](PF ₆) ₂	$V = 6571 (2) \text{ \AA}^3$
$M_r = 779.07$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 16.498 (3) \text{ \AA}$	$\mu = 0.86 \text{ mm}^{-1}$
$b = 16.912 (3) \text{ \AA}$	$T = 293 \text{ K}$
$c = 23.552 (5) \text{ \AA}$	$0.35 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Oxford Gemini S Ultra diffractometer	54743 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	6441 independent reflections
$T_{\min} = 0.753$, $T_{\max} = 0.847$	5187 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	443 parameters
$wR(F^2) = 0.169$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$
6441 reflections	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

All H atoms were placed geometrically, with C—H = 0.93 (aromatic) or 0.96 \AA (CH₂) and N—H = 0.86–0.91 \AA , and refined using a riding-atom model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The remaining

H atoms were located in difference Fourier maps. For (II), disordered atoms F5 and F6 were set as two sites with the respective occupancies summing to unity [final refined occupancies = 0.52 (3):0.48 (3) for F5 and 0.551 (16):0.449 (16) for F6].

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *enCIFer* (Macrae *et al.*, 2006).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: YF3005). Services for accessing these data are described at the back of the journal.

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