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copper(II)) bis(hexafluorophosphate)**

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Di- μ -methoxy-bis($\{N,N'$ -bis[2-(3,5-dimethylpyrazol-1-yl)ethyl]amine- κ^3N }-copper(II)) bis(hexafluorophosphate)

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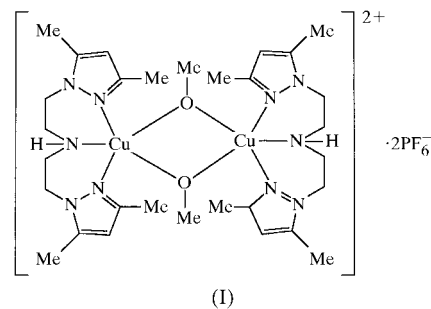
Data validation number: IUC0000295

The title compound, $[\text{Cu}_2(\text{C}_{14}\text{H}_{23}\text{N}_5)_2(\text{CH}_3\text{O})_2](\text{PF}_6)_2$, has a doubly methoxy-bridged centrosymmetric copper dimer cation involving two tridentate bis(pyrazolyl)amine ligands. The geometry of each Cu^{II} atom is a distorted square pyramid with two N atoms of the pyrazole in bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (bpea) and two μ_2 -bridging O atoms of the methoxy ligands forming the basal plane, and the amine N atom occupying the axial position. In the bridging plane, the Cu—O bond lengths are 1.940 (4) and 1.942 (4) Å, and the bond angles for O—Cu—O and Cu—O—Cu are 76.1 (2) and 103.9 (2)°, respectively. The Cu...Cu distance is 3.058 (1) Å. The central four-membered ring lies on an inversion centre.

Comment

Copper plays an important role in a variety of biological functions as an essential trace element (Kaim & Rall, 1996). The copper ions as centres of the active site in metalloproteins are involved in biological processes like electron transfer, oxidation and dioxygen transport (Solomon *et al.*, 1992). A great number of transition metal complexes of poly-(pyrazolyl)borate (Trofimenko, 1993) and pyrazole-based chelating ligands (Mukherjee, 2000) have been found in coordination chemistry. However, the bis(pyrazolylethyl)-amine derivative is rare in spite of the extensive studies for various nitrogen heterocyclic ligand systems (Sorrell & Malachowski, 1983; Martens *et al.*, 1995). The Cu^{I} compound of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine was investigated as well as that of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether having the unsaturated T-shape arrangement (Sorrell & Malachowski, 1983), but its crystal structure was not explored. More recently, the mononuclear Cu^{II} complexes of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine involving T-shape and square pyramidal coordination geometry were prepared and their structures have been characterized (Martens *et al.*, 1995), but their dicopper(II) complexes have not been reported yet. In this context, we report the crystal structure of the title compound, (I), as an extension of the doubly methoxy-

bridged dimeric copper complex type. The title compound consists of doubly methoxy-bridged dinuclear copper(II) units, two bpea ligands and two hexafluorophosphates.



The dinuclear unit has a centre of symmetry at the midpoint of the bridging plane. The Cu—Cuⁱ [symmetry code: (i) $-x, 2 - y, -z$] distance [3.058 (1) Å] is slightly longer than the values in the range 2.970 (7)–3.037 (2) Å in analogous methoxy-bridged copper(II) complexes (Willett & Breneman, 1983; Drew *et al.*, 1988; van Albada *et al.*, 1995, 1997; Komaei *et al.*, 1999). In the bridging plane, bond lengths of Cu—O1 and Cu—O1ⁱ are 1.940 (4) and 1.942 (4) Å, and bond angles of O1—Cu—O1ⁱ and Cu—O1—Cuⁱ are 76.1 (2) and 103.9 (2)°, respectively. Each copper ion is five-coordinate, surrounded by three N atoms of bpea and two O atoms of methoxy. The coordination geometry around each Cu atom is described as a distorted square pyramid. In the title compound, the N atom of each pyrazole in bpea and μ_2 -bridging O atom in each methoxy are in the equatorial positions with bond angles ranging between 76.1 (2) and 94.4 (2)°, whereas N atom of amine in bpea is in the axial position. The Cu—N bond lengths [1.991 (5)–2.317 (5) Å] are slightly longer than those [1.923 (1)–2.075 (8) Å] in the related mononuclear copper complexes (Martens *et al.*, 1995); these values are consistent with the distances between copper and typical σ -donor nitrogen heterocyclic rings. Each amine N atom is in an axial position *trans* to the equatorial plane containing N atom of each pyrazole in bpea and O atom of each methoxy. The Cu—N(amine) [2.317 (5) Å] bond distance of the axial position, due to an elongation of Jahn–Teller effect, is about 0.309 Å longer than Cu—N(pyrazole) bond distances [average 2.009 (5) Å] in the equatorial plane.

Experimental

All chemicals were purchased from Aldrich and used as received. All reactions were performed under argon using standard Schlenk technique and the solvents were freshly distilled prior to use. Elemental analyses were carried out on a FIFONS, EA 1110/EA1108 by Chemical Analysis Laboratory of Korea Basic Science Institute at Kyungpook National University. To a solution of 5 g (0.019 mol) of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (bpea), prepared according to the synthetic procedures of Sorrell and Martens groups (Sorrell & Malachowski, 1983; Martens *et al.*, 1995), in 200 ml of acetonitrile was added slowly 7.13 g (0.019 mol) of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$, prepared by the method of Kubas (1979) and the mixture was stirred for 5 days at room temperature. The white solid was precipitated within 1 day and the resulting solid was filtered off and

dried *in vacuo*. The white solid (7.87 g) was dissolved in 50 ml of methanol, the solution was rapidly converted to dark green and was left to stand at room temperature for several days to afford the green crystals. Yield: 8.45 g (82% based on copper atom). Analysis calculated for $C_{30}H_{52}N_{10}O_2Cu_2P_2F_{12}$: C 35.97, H 5.23, N 13.98%; Found: C 36.12, H 5.16, N 13.98%.

Crystal data

$[Cu_2(C_{14}H_{23}N_5)_2(CH_3O)_2](PF_6)_2$
 $M_r = 1001.86$
 Orthorhombic, *Pbca*
 $a = 15.1607 (7) \text{ \AA}$
 $b = 12.7860 (9) \text{ \AA}$
 $c = 23.316 (1) \text{ \AA}$
 $V = 4519.7 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.472 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.8\text{--}12.5^\circ$
 $\mu = 1.101 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Tetragonal rod, green
 $0.40 \times 0.30 \times 0.30 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 4256 measured reflections
 4174 independent reflections
 2065 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.0071$

$\theta_{max} = 25.47^\circ$
 $h = 0 \rightarrow 18$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 28$
 2 standard reflections
 frequency: 60 min
 intensity decay: 0.2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.189$
 $S = 1.380$
 4174 reflections
 255 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0720P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.014$
 $\Delta\rho_{max} = 0.98 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.53 \text{ e \AA}^{-3}$

A C atom of the methyl group at pyrazole and all F atoms were disordered, and were refined with isotropic displacement parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD* (McArdle, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

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