

axial bond length Cu—S = 2.635 (2) Å and Cu...O = 2.554 (4) Å. The short Cu—S bond distance in the present complex and the strong distortion of the basal plane show clearly that the ligand Lpy₂ adopts a rather strained conformation. [CuLpy₂]²⁺ has the crystallographically required mirror symmetry. But C(7), C(8), and to a much lesser extent C(9) are statistically disordered, manifested by large anisotropic thermal parameters approximately rectangular to their respective chelate rings. One has to assume, therefore, that the conformation of the chelate rings is either λλλ or δδδ. The macrocycle then adopts the [333] conformation. A similar situation is frequently observed for 1,4,7-triazacyclononane complexes (Drüeke, Wiegardt, Nuber & Weiss, 1989).

References

- CRAIG, A., PARKER, D. & FERGUSON, G. (1989). *Acta Cryst.* **C45**, 1498–1500.
 DRÜEKE, ST., WIEGHARDT, K., NUBER, B. & WEISS, J. (1989). *Inorg. Chem.* **28**, 1414–1417.
 FORTIER, D. G. & MCAULEY, A. (1989). *Inorg. Chem.* **28**, 655–662.
 HARTMANN, J. R. & COOPER, S. R. (1986). *J. Am. Chem. Soc.* **108**, 1202–1205.
 HOFFMANN, P., HERMES, F.-J. & MATTES, R. (1988). *Z. Naturforsch. Teil B*, **43**, 567–570.
 HOFFMANN, P. & MATTES, R. (1988). *Z. Naturforsch. Teil B*, **43**, 261–264.
 HOFFMANN, P. & MATTES, R. (1989). *Inorg. Chem.* **28**, 2092–2096.
 HOFFMANN, P., STEINHOFF, A. & MATTES, R. (1987). *Z. Naturforsch. Teil B*, **42**, 867–873.
 SHELDRIK, G. M. (1989). *SHELXTL-Plus* for Siemens R3m Crystallographic Research Systems. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

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Synthesis and Structure of Aquabis(2,2'-bipyrimidine-*N,N'*)copper(II) Hexafluorophosphate Dihydrate

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Abstract. [Cu(C₈H₆N₄)₂(H₂O)](PF₆)₂·2H₂O, *M_r* = 723.84, monoclinic, *I*2/*c*, *a* = 18.862 (2), *b* = 7.699 (1), *c* = 17.090 (2) Å, β = 95.44 (2)°, *V* = 2470.6 (5) Å³, *Z* = 4, *D_x* = 1.95 g cm⁻³, *Mo Kα*, λ = 0.71069 Å, μ = 10.9 cm⁻¹, *F*(000) = 1444, *T* = 298 K, final *R* = 0.039 and *wR* = 0.039 for 1833 reflections with *I* > 3σ(*I*). The compound is formed by [Cu(2,2'-bipyrimidine)₂(H₂O)]²⁺ cationic units, uncoordinated PF₆⁻ anions and crystallization water molecules. The Cu atom is coordinated to four N atoms of two bipyrimidine molecules and to an O atom of a water molecule in a distorted trigonal bipyramidal geometry. The bipyrimidine acts as a bidentate ligand.

Introduction. Polynuclear complexes, which contain ligands able to act as bridges between paramagnetic centers, have been studied during the last two decades in order to correlate structure and magnetic properties (Gatteschi, Kahn & Willett, 1985). The 2,2'-bipyrimidine ligand (bpm) is able to form magnetically coupled systems and, for this reason, particular attention was devoted to the synthesis of their metal complexes (Brewer & Sinn, 1985; Brewer, Murphy & Petersen, 1987; Kaim & Kholmann, 1987). Fe^{II} and Cu^{II} bipyrimidine (bpm) mixed complexes have been studied as models for binuclear metalloenzyme centers (Petty, Welch, Wilson, Bottomley & Kadish, 1980). We examined the

behaviour of this ligand with CuX_2 salts and we found that different complexes may be obtained. The bpm can act as a bis-bidentate ligand with CuX_2 salts when $X = \text{Cl}, \text{Br}, \text{NO}_3, \text{NCS}$ or NCO (De Munno & Bruno, 1984; Julve, De Munno, Bruno & Verdaguer, 1988; De Munno, Bruno, Julve, Verdaguer & Real, 1990). In this case all N atoms are involved in metal coordination, the bpm acting as a molecular bridge, and polymeric compounds were obtained. Alternatively the bpm can act as a bidentate ligand when $X = \text{SCN}$ leading to a linear-chain compound (De Munno *et al.*, 1990). Three different complexes, a mononuclear, a binuclear and a one-dimensional chain, can be isolated when $X = \text{ClO}_4$ (De Munno, Bruno, Dapporto, Julve & Verdaguer, 1988). In the mononuclear compound bpm is bidentate, whereas it is bis-bidentate in the dimeric and the polymeric ones, but in two different ways from those previously reported. In an attempt to study the influence of the counterion X on the resulting structure and consequently on the magnetic properties in Cu^{II} -bipyrimidine complexes, we synthesized the $[\text{Cu}(\text{H}_2\text{O})(\text{bpm})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ complex. Its structure is reported herein and compared to that of the parent $[\text{Cu}(\text{H}_2\text{O})(\text{bpm})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ complex.

Experimental. All the starting products were pure reagents and used as received. 2 mmol of KPF_6 dissolved in a minimum amount of water were added to an aqueous solution (30 ml) of 1 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 1 mmol of bpm. Green powder and polyhedral blue crystals are obtained as products by slow evaporation at room temperature. Analytical data (C, H, N and P) support formulae $[\text{Cu}_2(\text{C}_8\text{H}_6\text{N}_4)_3](\text{PF}_6)_4$ and $[\text{Cu}(\text{C}_8\text{H}_6\text{N}_4)_2](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$ for green and blue solids respectively.

A rhombic blue crystal of $0.12 \times 0.15 \times 0.11$ mm was used for intensity data collection. Accurate unit-cell dimensions and the crystal orientation matrix were obtained from least-squares refinement of 20 strong reflections in the $14 < 2\theta < 30^\circ$ range. Philips four-circle diffractometer, ω - 2θ scan technique, graphite-monochromated $\text{Mo K}\alpha$ radiation, scan range $2\theta = 3$ – 50° ($\overline{14} \leq h \leq 14, \overline{14} \leq k \leq 14, 0 \leq l \leq 8$). No systematic loss of intensity of three standard reflections ($3\overline{6}2, \overline{2}23, 314$) was observed during data collection. Assuming $P\overline{1}$ symmetry, 4302 reflections were measured (3907 unique), and Lorentz and polarization corrections applied to the intensity data, absorption and extinction corrections being ignored. Symmetry was checked by means of the Le Page method (Spek, 1988) which revealed a monoclinic cell. Assuming the spatial group $I2/c$, 1978 reflections were unique, $R_{\text{int}} = 0.019$. The structure was solved by Patterson and Fourier techniques; 1833 reflections having $I > 3\sigma(I)$ were used to refine 191 parameters by a full-matrix least-squares procedure, $\sum w(|F_o| -$

$|F_c|)^2$ minimized. All non-H atoms were refined anisotropically, while H atoms of the water molecules and other H atoms, from ΔF map and calculated positions respectively, were included with a common thermal parameter. Final $R = 0.039$, $wR = 0.039$, unit weights were used, $S = 2.267$, max. $\Delta/\sigma = 0.003$, max. and min. $\Delta\rho$ excursions in ΔF synthesis 0.58 and 0.15 e \AA^{-3} respectively. Scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974), and for H atoms from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974). All calculations were performed with *SHELX76* (Sheldrick, 1976) and the *PARST* (Nardelli, 1983) set of programs on the VAX/VMS computer of the Università della Calabria and IBM 3090/120S computer of the Università di Messina.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, bond lengths and angles in Table 2, possible hydrogen bonds in Table 3.* The Cu atom is in a penta-coordinate geometry, being bonded to N atoms of two bpm ligands that act in a bidentate fashion, and to an O atom of a water molecule as shown in Fig. 1. A C_2 symmetry operation around the Cu—O(1) axis produces the second bpm molecule (symmetry code: $-x, y, 1-z$). This forms with the first molecule a dihedral angle of $104.4(1)^\circ$. The structure is similar to those reported for the Cu-bipyridine complexes (Harrison, Kennedy, Power, Sheahan & Hataway, 1981). The structure of the title compound is similar to one of formula $[\text{Cu}(\text{H}_2\text{O})(\text{bpm})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, that we have previously studied (De Munno *et al.*, 1988); the N(1)—Cu—O(1) and N(1a)—Cu—O(1) angles are different from the corresponding ones in the Cu^{II} -bipyridine compounds. In fact, for such a family of complexes a distortion towards a square-based pyramidal geometry was observed, the O atom tending to occupy the apical position, whereas in the 2,2'-bipyrimidine parent complexes a distortion in the opposite direction occurs. The Cu—O(1) distance is $1.982(5) \text{ \AA}$ and the N(1)—Cu—O(1) angle is $128.6(1)^\circ$ [the corresponding values in the Cu-bipyrimidine perchlorate compound are $1.972(5) \text{ \AA}$ and $130.0(1)^\circ$]. The N(1), N(3), Cu and N(3a) atoms are in a planar arrangement in both complexes. This plane forms with the N(1), Cu, N(1a), O(1) plane a dihedral angle of $97.5(1)^\circ$. Bond distances and angles in the bpm ligand are close to those found in

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52995 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic (Hamilton, 1959) thermal parameters ($\text{\AA}^2 \times 10^3$) for non-H atoms

	x	y	z	U_{eq}
Cu	0	959 (1)	2500	30 (1)
N(1)	666 (1)	2644 (4)	3178 (2)	29 (1)
N(2)	823 (2)	3812 (4)	4472 (2)	36 (1)
N(3)	-495 (1)	997 (4)	3481 (2)	29 (1)
N(4)	-382 (2)	1963 (4)	4805 (2)	35 (1)
C(1)	1213 (2)	3593 (5)	2973 (2)	37 (1)
C(2)	1574 (2)	4707 (5)	3497 (2)	42 (1)
C(3)	1369 (2)	4747 (5)	4253 (2)	40 (1)
C(4)	488 (2)	2836 (5)	3917 (2)	28 (1)
C(5)	-163 (2)	1878 (5)	4089 (2)	29 (1)
C(6)	-981 (2)	1103 (6)	4913 (2)	39 (1)
C(7)	-1362 (2)	181 (6)	4324 (2)	40 (1)
C(8)	-1099 (2)	147 (5)	3597 (2)	36 (1)
O(1)	0	-1615 (6)	2500	55 (2)
O(2)	-376 (2)	-3572 (5)	3709 (2)	53 (1)
P(1)	-2496 (5)	-4675 (2)	3642 (6)	38 (1)
F(1)	-2856 (2)	-6028 (4)	4158 (2)	81 (1)
F(2)	-2592 (2)	-5863 (5)	2897 (2)	83 (1)
F(3)	-2108 (2)	-3287 (5)	3154 (2)	98 (2)
F(4)	-2445 (2)	-3386 (4)	4358 (2)	81 (1)
F(5)	-3263 (2)	-3870 (5)	3361 (2)	89 (1)
F(6)	-1741 (2)	-5484 (5)	3892 (2)	83 (1)

Table 2. Bond lengths (\AA) and interbond angles ($^\circ$)

Cu—N(1)	2.080 (3)	C(5)—N(3)	1.345 (4)
Cu—N(3)	1.994 (3)	N(4)—C(6)	1.338 (5)
Cu—O(1)	1.982 (5)	C(6)—C(7)	1.378 (5)
N(1)—C(1)	1.339 (5)	C(7)—C(8)	1.382 (5)
C(1)—C(2)	1.373 (5)	C(8)—N(3)	1.345 (5)
C(2)—C(3)	1.383 (6)	P(1)—F(1)	1.560 (3)
C(3)—N(2)	1.340 (5)	P(1)—F(2)	1.565 (3)
N(2)—C(4)	1.324 (4)	P(1)—F(3)	1.577 (4)
C(4)—N(1)	1.344 (4)	P(1)—F(4)	1.570 (3)
C(4)—C(5)	1.486 (5)	P(1)—F(5)	1.606 (3)
C(5)—N(4)	1.330 (4)	P(1)—F(6)	1.576 (3)
N(1)—Cu—O(1)	128.6 (1)	C(6)—C(7)—C(8)	117.4 (4)
N(1)—Cu—N(1a)	102.8 (1)	C(7)—C(8)—N(3)	120.4 (3)
N(1)—Cu—N(3a)	98.8 (1)	C(8)—N(3)—C(5)	118.1 (3)
N(1)—Cu—N(3)	80.1 (1)	C(8)—N(3)—Cu	126.0 (2)
O(1)—Cu—N(3)	90.8 (1)	C(5)—N(3)—Cu	115.8 (2)
N(3)—Cu—N(3a)	178.3 (1)	F(1)—P(1)—F(2)	92.7 (2)
Cu—N(1)—C(1)	129.4 (2)	F(1)—P(1)—F(5)	90.0 (2)
Cu—N(1)—C(4)	113.6 (2)	F(1)—P(1)—F(4)	88.9 (2)
C(1)—N(1)—C(4)	116.9 (3)	F(1)—P(1)—F(6)	90.8 (2)
N(1)—C(1)—C(2)	121.1 (3)	F(1)—P(1)—F(3)	177.4 (2)
C(1)—C(2)—C(3)	117.3 (4)	F(2)—P(1)—F(5)	87.1 (2)
C(2)—C(3)—N(2)	122.7 (4)	F(2)—P(1)—F(4)	175.5 (2)
C(3)—N(2)—C(4)	115.6 (3)	F(2)—P(1)—F(6)	91.2 (2)
N(2)—C(4)—N(1)	126.3 (3)	F(2)—P(1)—F(3)	89.4 (2)
N(1)—C(4)—C(5)	114.5 (3)	F(5)—P(1)—F(4)	88.7 (2)
N(2)—C(4)—C(5)	119.1 (3)	F(5)—P(1)—F(6)	178.2 (2)
C(4)—C(5)—N(4)	119.5 (3)	F(5)—P(1)—F(3)	91.7 (2)
C(4)—C(5)—N(3)	115.5 (3)	F(4)—P(1)—F(6)	93.0 (2)
N(3)—C(5)—N(4)	125.0 (3)	F(4)—P(1)—F(3)	89.2 (2)
C(5)—N(4)—C(6)	116.3 (3)	F(6)—P(1)—F(3)	87.6 (2)
N(4)—C(6)—C(7)	122.9 (3)		

the series Cu₂(bpm)₂X₄ (X = Cl, Br, NO₃, NCO or NCS). The differences occur because the bpm ligand acts in a bidentate fashion in the PF₆ and ClO₄ compounds and in a bis-bidentate fashion in the other complexes. So N(2)—C(4)—C(5), N(4)—C(5)—C(4) angles are larger than N(1)—C(4)—C(5) and N(3)—C(5)—C(4). The bipyrimidine rings are

Table 3. Bond distances (\AA) and angles ($^\circ$) of possible hydrogen bonds (B...H—A).

B...H—A	B...A	B...H	H—A	B...H—A
O(1)—H(1w)...O(2)	2.705 (4)	1.94 (5)	1.01 (1)	174 (5)
O(2)—H(3w)...F(6)	3.007 (5)	2.31 (5)	1.01 (1)	159 (5)

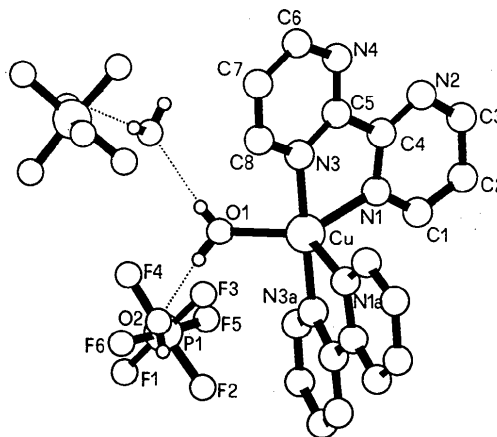


Fig. 1. View of the [Cu(H₂O)(C₈H₆N₄)₂](PF₆)₂·2H₂O complex.

planar, forming a dihedral angle of 6.7 (1) $^\circ$ [6.2 (1) $^\circ$ in the analogous ClO₄ compound].

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References

- BREWER, G. & SINN, E. (1985). *Inorg. Chem.* **24**, 4580–4584.
- BREWER, K. J., MURPHY, W. R. & PETERSEN, J. D. (1987). *Inorg. Chem.* **26**, 3376–3379.
- DE MUNNO, G. & BRUNO, G. (1984). *Acta Cryst.* **C40**, 2030–2032.
- DE MUNNO, G., BRUNO, G., DAPPORTO, P., JULVE, M. & VERDAGUER, M. (1988). *Z. Kristallogr.* **325**, 185.
- DE MUNNO, G., BRUNO, G., JULVE, M., VERDAGUER, M. & REAL, J. A. (1990). In preparation.
- GATTESCHI, D., KAHN, O. & WILLETT, R. D. (1985). Editors, *Magneto-Structural Correlations in Exchange Coupled Systems*. NATO ASI Series, Vol. C140. Dordrecht: Reidel.
- HARRISON, W. D., KENNEDY, D. M., POWER, M., SHEAHAN, R. & HATAWAY, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1556–1564.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99 and 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JULVE, M., DE MUNNO, G., BRUNO, G. & VERDAGUER, M. (1988). *Inorg. Chem.* **27**, 3160–3165.
- KAIM, W. & KholmANN, S. (1987). *Inorg. Chem.* **26**, 68–77.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- PETTY, R. H., WELCH, B. R., WILSON, L. J., BOTTOMLEY, L. A. & KADISH, K. M. (1980). *J. Am. Chem. Soc.* **102**, 611–620.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SPEK, A. L. (1988). *J. Appl. Cryst.* **21**, 578–579.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.