

Coordination Geometries in Bis(di-2-pyridylamine)copper(II) Complexes. Crystal Structures of $[\text{CuL}_2](\text{PF}_6)_2$, $[\text{CuL}_2(\text{NO}_3)_2]$ and $[\text{CuL}_2(\text{NCS})_{1.5}(\text{ClO}_4)_{0.5}][\text{CuL}_2(\text{NCS})_2(\text{ClO}_4)_2]$ (L = Di-2-pyridylamine)

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The crystal structures of three compounds containing bis(di-2-pyridylamine)-copper(II) complex units have been determined by X-ray crystallographic methods; $[\text{Cu}(\text{dpa})_2](\text{PF}_6)_2$ (**1**), $[\text{Cu}(\text{dpa})_2(\text{NO}_3)_2]$ (**2**) and $[\text{Cu}(\text{dpa})_2(\text{NCS})_{1.5}(\text{ClO}_4)_{0.5}][\text{Cu}(\text{dpa})_2(\text{NCS})_2(\text{ClO}_4)_2]$ (**3**). Compound **1** crystallizes in space group *Fddd* with cell dimensions $a = 9.418(2)$, $b = 13.472(3)$, $c = 40.834(5)$ Å; compound **2** in space group *P2₁/c* with $a = 8.413(2)$, $b = 17.096(2)$, $c = 7.603(1)$ Å, $\beta = 94.18(1)^\circ$; compound **3** in space group *P2₁/c* with cell dimensions $a = 12.758(1)$, $b = 14.459(2)$, $c = 19.397(3)$ Å, $\beta = 93.81(1)^\circ$. The structures were refined by full-matrix least-squares methods to *R*-values of 0.049, 0.031 and 0.060 for compounds **1**, **2** and **3**, respectively, using 1110, 1631 and 4760 reflections collected at room temperature with monochromated MoK α radiation. In compound **1** the anions are uncoordinated, and the complex features the compressed tetrahedral geometry. In compound **2** the complex unit is centrosymmetric and octahedrally elongated, with the anions coordinating in axial positions. Two crystallographically independent molecules are found in compound **3**, one complex unit being centrosymmetric and octahedrally elongated, the other close to square-based pyramidal with one of the dipyridylamine ligands occupying the apical and one of the equatorial positions.

Copper(II) complexes are known to display a large variation of non-regular stereochemistries.¹ Small changes in ligands and/or counter-ions may often give rise to considerable differences in coordination geometry. A large number of CuL_2XY compounds, with L being 2,2'-bipyridyl (bpy) and X, Y various counter-ions, coordinated or not, have been investigated.^{2–4} Structural data are more limited for corresponding complexes in which L is the more flexible di-2-pyridylamine chelate (dpa).^{5–11} The present paper reports the crystal structures of three compounds of this family. During the course of the work we realized that some preliminary data on compound **3** have been given in the literature,¹² but no full report has, to our knowledge, appeared previously.

Experimental

Syntheses. $[\text{CuL}_2](\text{PF}_6)_2$ (**1**) was originally obtained as a side product in a synthesis aimed at producing a binuclear dithiooxamido-bridged Cu-complex with

di-2-pyridylamine as outer ligand. In a subsequent synthesis the more rational method of Lancaster *et al.* was used.¹³ For preparing the other two compounds the methods given by McWhinnie¹⁴ for $[\text{CuL}_2(\text{NO}_3)_2]$ (**2**) and $[\text{CuL}_2(\text{NCS})](\text{ClO}_4)$ were followed. Although the synthesis in the latter case also appeared to proceed as described by these authors, and the IR spectrum was similar to the reported one, the X-ray analysis later revealed a different ratio between NCS^- and ClO_4^- ions (see below), the composition of **3** being best described by the formula $[\text{CuL}_2(\text{NCS})_{1.5}(\text{ClO}_4)_{0.5}][\text{CuL}_2(\text{NCS})_2(\text{ClO}_4)_2]$.

Anal. Found: C, 46.7; H, 3.4; N, 17.4; O, 9.0; S, 6.2. Calc. for $\text{Cu}_3\text{Cl}_{2.5}\text{S}_{3.5}\text{O}_{10}\text{N}_{21.5}\text{C}_{63.5}\text{H}_{54}$, which is the composition inferred from X-ray data: C, 45.7; H, 3.3; N, 18.0; O, 9.6; S, 6.7.

X-Ray data collection and structure determinations. Information concerning crystal data, experimental conditions and refinement results are summarized in Table 1. During each data collection three reference reflections were monitored and showed no sign of crystal deterioration.

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Table 1. Crystallographic data for [CuL₂](PF₆)₂ (1), [CuL₂(NO₃)₂] (2) and [CuL₂(NCS)_{1.5}(ClO₄)_{0.5}][CuL₂NCS]₂(ClO₄)₂ (3).

	Compound 1	Compound 2	Compound 3
Chemical formula	CuP ₂ F ₁₂ N ₆ C ₂₀ H ₁₈	CuO ₆ N ₈ C ₂₀ H ₁₈	Cu ₃ Cl _{2.5} S _{3.5} O ₁₀ N _{21.5} C _{63.5} H ₅₄
FW	695.88	529.96	1649.07
Space group	<i>Fddd</i> (No. 70)	<i>P2₁/c</i> (No. 14)	<i>P2₁/c</i> (No. 14)
<i>a</i> /Å ^a	9.418(2)	8.413(2)	12.758(1)
<i>b</i> /Å	13.472(3)	17.096(2)	14.459(2)
<i>c</i> /Å	40.834(5)	7.603(1)	19.397(3)
β/°		94.18(1)	93.81(1)
<i>V</i> /Å ³	5181(3)	1090.6(5)	3570(1)
<i>Z</i>	8	2	2
<i>D_x</i> /Mg m ⁻³	1.784	1.614	1.553
<i>T</i> /K	293	294	294
Instrument	CAD4	CAD4	CAD4
λ/Å	0.71073	0.71073	0.71073
Crystal size/mm	0.40 × 0.40 × 0.17	0.70 × 0.24 × 0.11	0.22 × 0.13 × 0.07
μ/mm ⁻¹	1.073	1.056	1.150
Max., min. transmission factors	1.607, 0.542 ^b	0.985, 0.636 ^c	1.182, 0.992 ^b
<i>F</i> (000)	2776	542	1702
Max. 2θ/°	56	50	50
Scan type	ω	ω	ω
Scan range/°	0.70 + 0.347 tan θ	1.20 + 0.347 tan θ	1.00 + 0.347 tan θ
Speed/° min ⁻¹	2.0	2.67	2.67
Reflections collected	<i>hkl</i>	<i>hk ± l</i>	<i>hk ± l</i>
Unique reflections	1569	1896	6201
Reflections in refinement	1110 [<i>I</i> > 3σ(<i>I</i>)]	1631 [<i>I</i> > 2σ(<i>I</i>)]	4760 [<i>I</i> > 2σ(<i>I</i>)]
Parameters refined	96	197	471
Functions minimized	Σ[<i>w</i> (<i>F_o</i> - <i>F_c</i>) ²]	Σ[<i>w</i> (<i>F_o</i> - <i>F_c</i>) ²]	Σ[<i>w</i> (<i>F_o</i> - <i>F_c</i>) ²]
<i>R</i> ^d	0.049	0.031	0.060
<i>R_w</i> ^e	0.061	0.037	0.059
<i>S</i> ^f	3.35	2.42	3.23
<i>k</i> in weighting scheme ^g	0.02	0.02	0.02
Max. shift/esd	0.02	0.05	0.34
Largest residual peak/e Å ⁻³	0.52	0.46	2.00 ^h
Lowest residual peak/e Å ⁻³	-0.31	-0.48	-1.22 ^h

^aCell dimensions are calculated from a least-squares fit of the setting angles of 25 reflections with 2θ in the region 10–20° (compound 1), 18–42° (compound 2) and 36–48° (compound 3). ^bEmpirical absorption correction.¹⁷ ^cAbsorption correction by the gaussian integration method.¹⁸ ^d $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^e $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$. ^f $S = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$. ^g $w = 4F_o^2 / [\sigma_c^2 + (kF_o^2)^2]$, where σ_c is the standard deviation in F^2 based on counting statistics alone. ^hResidual density situated in the region of the disordered NCS⁻ ion.

The F-centred orthorhombic cell of **1** may be transformed to a C-centered monoclinic cell with cell dimensions (9.42 Å, 13.47 Å, 20.96 Å, 103.0°) similar to those of the corresponding perchlorate (9.35 Å, 12.88 Å, 19.69 Å, 102.8°).⁵ Intensity measurements of 200 reflections in four octants did not, however, reveal deviation from *mmm* symmetry, and systematic extinctions were consistent with three mutually perpendicular diamond glide planes. The subsequent structure determination demonstrated a significant difference in the crystalline packing of the PF₆⁻ and ClO₄⁻ salts.

The structures were solved by the Patterson method (compound **1**) and by direct methods (compounds **2** and **3**) and were refined by the full-matrix least-squares method. In **3** a disorder in the anion weakly coordinated to CuI caused some problems during the refinement procedure. The major peaks in the difference Fourier map were consistent with NCS⁻ coordinated through nitrogen. Refinement of this ion gave, however, an extraordinary low temperature factor on the carbon atom

and high factors for the terminal N and S atoms. The residual electron density peaks at this point suggested that the position could be partly occupied by a ClO₄⁻ ion. Attempts to refine the two anions were made in alternate cycles. The occupancy factors of the individual atoms indicated a ratio of approximately 3 : 1 for NCS/ClO₄ in this site. In the final refinement cycles occupancies were held fixed at 0.75 and 0.25, respectively. Introducing the fractional ClO₄⁻ ion into the model caused the *R*-value to drop from 0.080 to 0.060.

Non-hydrogen atoms, except those in the disordered region of **3**, were anisotropically refined. Hydrogen atoms were included and fixed at calculated positions in **1** and **3**. In **2** they were localized in a difference map and refined isotropically. Refinement converged at *R* = 0.049, 0.031 and 0.060 for **1**, **2** and **3**, respectively. All calculations were carried out with the Enraf-Nonius Structure Determination Programs.¹⁵ The scattering curves, with anomalous scattering terms included, were those of Cromer and Mann.¹⁶

Results

Coordinates and isotropically equivalent displacement parameters are listed in Tables 2–4 and bond distances and angles involving non-hydrogen atoms in Tables 5–7. The complex units are shown in Fig. 1, 3 and 5 and packing diagrams in Fig. 2, 4 and 6. Supplementary material includes coordinates of H-atoms, anisotropic thermal parameters, bond distances and angles involving H-atoms, equations of least-squares planes with atomic

deviations, and structure factor tables; all are available from the authors on request.

Description of Structure 1. The crystal structure comprises discrete $\text{Cu}(\text{dpa})_2^{2+}$ (Fig. 1) and PF_6^- ions. The copper ion, situated at a position with 222 symmetry,

Table 2. Atomic parameters for compound 1, $[\text{CuL}_2](\text{PF}_6)_2$.

Atom	x	y	z	$B(\text{eq})/\text{\AA}^2$ ^a
Cu1	0.500	0.500	0.500	3.34(2)
P1	0.500	0.500	0.32014(3)	4.15(3)
F1	0.6092(4)	0.4672(2)	0.34740(7)	9.24(9)
F2	0.3903(3)	0.5338(2)	0.29400(7)	7.83(8)
F3	0.4335(3)	0.3933(2)	0.31914(8)	8.05(8)
N1	0.6344(3)	0.5498(3)	0.46736(7)	3.64(6)
N2	0.500	0.500	0.4223(1)	4.1(1)
C2	0.6155(4)	0.5459(3)	0.43515(8)	3.73(8)
C3	0.7122(5)	0.5876(4)	0.4139(1)	5.8(1)
C4	0.8328(5)	0.6322(5)	0.4265(1)	7.1(1)
C5	0.8498(5)	0.6384(4)	0.4585(1)	6.7(1)
C6	0.7521(5)	0.5973(3)	0.47903(9)	5.06(9)

^aThe isotropic equivalent displacement parameter is defined as $B(\text{eq}) = 4/3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 3. Atomic parameters for compound 2, $[\text{CuL}_2(\text{NO}_3)_2]$.

Atom	x	y	z	$B(\text{eq})/\text{\AA}^2$
Cu	0.000	0.500	0.000	2.195(7)
O31	-0.2017(2)	0.4026(1)	-0.1067(2)	3.19(4)
O32	-0.2986(3)	0.2910(1)	-0.1833(4)	6.26(6)
O33	-0.0474(2)	0.3066(1)	-0.1660(3)	4.34(4)
N1A	-0.0916(2)	0.4866(1)	0.2359(3)	2.30(4)
N1B	0.1668(2)	0.4233(1)	0.0909(3)	2.18(4)
N2AB	-0.0239(2)	0.3536(1)	0.2372(3)	2.55(4)
N3	-0.1834(3)	0.3331(1)	-0.1509(3)	2.87(4)
C2A	-0.1121(3)	0.4144(1)	0.2980(3)	2.24(4)
C2B	0.1259(3)	0.3590(1)	0.1766(3)	2.24(5)
C3A	-0.2184(3)	0.3991(2)	0.4259(3)	2.96(5)
C3B	0.2334(3)	0.2974(1)	0.2100(4)	3.15(5)
C4A	-0.2929(3)	0.4603(2)	0.5012(3)	3.48(6)
C4B	0.3850(3)	0.3042(2)	0.1594(4)	3.81(6)
C5A	-0.2623(3)	0.5357(2)	0.4478(3)	3.38(6)
C5B	0.4312(3)	0.3726(2)	0.0813(4)	3.55(6)
C6A	-0.1628(3)	0.5464(1)	0.3163(3)	2.88(5)
C6B	0.3210(3)	0.4297(1)	0.0494(3)	2.82(5)
H2AB	-0.046(2)	0.311(1)	0.267(3)	1.3(4)*
H3A	-0.234(3)	0.349(1)	0.453(3)	3.2(6)*
H3B	0.202(3)	0.254(1)	0.269(3)	3.3(6)*
H4A	-0.364(3)	0.448(2)	0.587(4)	4.6(7)*
H4B	0.455(3)	0.265(1)	0.178(3)	3.4(6)*
H5A	-0.306(3)	0.577(1)	0.502(3)	3.0(5)*
H5B	0.532(3)	0.379(1)	0.047(3)	3.2(6)*
H6A	-0.139(3)	0.595(1)	0.276(3)	2.5(5)*
H6B	0.343(3)	0.477(1)	-0.013(3)	1.9(5)*

*These atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B(\text{eq}) = 4/3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 4. Atomic parameters for compound 3, $[\text{CuL}_2(\text{NCS})_{1.5}\text{ClO}_4]_{0.5}[\text{CuL}_2(\text{NCS})_2(\text{ClO}_4)_2]$.

Atom	x	y	z	$B(\text{eq})/\text{\AA}^2$
Cu1	0.000	0.000	0.000	3.24(2)
Cu2	0.55929(4)	0.12992(4)	0.65468(3)	3.06(1)
Cl1	0.0419(1)	0.43062(9)	0.15129(8)	4.83(3)
Cl2	0.2586(4)	-0.1132(3)	-0.0119(2)	2.29(8)* ^a
S1	0.3595(2)	-0.1403(2)	0.0020(1)	6.76(5)* ^b
S2	0.6316(1)	-0.1884(1)	0.66780(7)	5.09(4)
O1	-0.0395(3)	0.3656(3)	0.1472(3)	8.3(1)
O2	0.1363(4)	0.3877(3)	0.1307(3)	7.8(1)
O3	0.0609(4)	0.4671(5)	0.2175(3)	12.0(2)
O4	0.0166(6)	0.5023(4)	0.1064(4)	14.7(2)
O5	0.296(1)	-0.075(1)	0.057(1)	6.7(5)* ^a
O6	0.251(2)	-0.205(2)	0.006(1)	10.8(7)* ^a
O7	0.365(2)	-0.119(2)	-0.050(1)	11.5(8)* ^a
O8	0.195(1)	-0.067(1)	-0.0442(9)	6.6(4)* ^a
N1A	0.0530(3)	0.1208(2)	-0.0361(2)	3.04(8)
N1B	0.0710(3)	0.0388(3)	0.0918(2)	2.84(8)
N1C	0.4708(3)	0.1220(3)	0.7368(2)	3.11(8)
N1D	0.6687(3)	0.2120(3)	0.7166(2)	3.55(9)
N1E	0.6274(3)	0.1157(3)	0.5652(2)	3.24(9)
N1F	0.4676(3)	0.2286(3)	0.6088(2)	3.25(8)
N2AB	0.0254(3)	0.1938(3)	0.0687(2)	3.71(9)
N2CD	0.6138(3)	0.1453(3)	0.8190(2)	3.99(9)
N2EF	0.4733(3)	0.1600(3)	0.4997(2)	3.86(9)
N3	0.1642(5)	-0.0680(4)	-0.0321(3)	5.0(1)* ^b
N4	0.6055(3)	0.0014(3)	0.6790(2)	4.4(1)
C2A	0.0437(4)	0.1988(3)	-0.0005(2)	3.3(1)
C2B	0.0617(4)	0.1257(3)	0.1142(2)	3.0(1)
C2C	0.5131(4)	0.1134(3)	0.8010(2)	3.3(1)
C2D	0.6788(4)	0.2050(3)	0.7849(3)	3.5(1)
C2E	0.5739(4)	0.1214(3)	0.5043(2)	3.4(1)
C2F	0.4352(3)	0.2271(3)	0.5423(2)	3.3(1)
C3A	0.0541(5)	0.2856(3)	-0.0305(3)	5.0(1)
C3B	0.0916(4)	0.1495(4)	0.1828(3)	4.0(1)
C3C	0.4575(4)	0.0730(4)	0.8536(3)	4.6(1)
C3D	0.7553(4)	0.2536(4)	0.8250(3)	5.3(1)
C3E	0.6150(4)	0.0887(4)	0.4442(3)	4.3(1)
C3F	0.3621(4)	0.2912(4)	0.5137(3)	4.2(1)
C4A	0.0849(5)	0.2904(4)	-0.0964(3)	6.0(2)
C4B	0.1345(4)	0.0847(4)	0.2262(2)	4.3(1)
C4C	0.3575(5)	0.0438(4)	0.8379(3)	5.5(1)
C4D	0.8212(4)	0.3128(4)	0.7916(4)	6.2(2)
C4E	0.7142(4)	0.0546(4)	0.4477(3)	5.0(1)
C4F	0.3285(4)	0.3603(4)	0.5541(3)	4.6(1)
C5A	0.1027(5)	0.2095(4)	-0.1324(3)	5.1(1)
C5B	0.1502(4)	-0.0044(4)	0.2023(2)	4.1(1)
C5C	0.3105(4)	0.0561(4)	0.7726(3)	5.4(1)
C5D	0.8091(5)	0.3218(4)	0.7213(3)	5.7(2)
C5E	0.7729(4)	0.0529(4)	0.5100(3)	4.9(1)
C5F	0.3670(4)	0.3661(4)	0.6224(3)	4.7(1)
C6A	0.0863(4)	0.1274(4)	-0.1014(2)	3.9(1)
C6B	0.1182(4)	-0.0240(3)	0.1357(2)	3.5(1)
C6C	0.3697(4)	0.0946(4)	0.7243(3)	4.2(1)
C6D	0.7329(4)	0.2725(4)	0.6859(3)	4.6(1)
C6E	0.7270(4)	0.0837(4)	0.5671(3)	4.3(1)
C6F	0.4343(4)	0.3001(4)	0.6481(3)	3.9(1)
C7	0.245(1)	-0.1095(9)	-0.0151(7)	11.6(4)* ^b
C8	0.6165(4)	-0.0767(4)	0.6747(2)	3.5(1)

^a and ^b denote atoms of multiplicity 0.25 and 0.75, respectively. *These atoms were refined isotropically. The isotropic equivalent thermal parameter is given as: $B(\text{eq}) = 4/3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

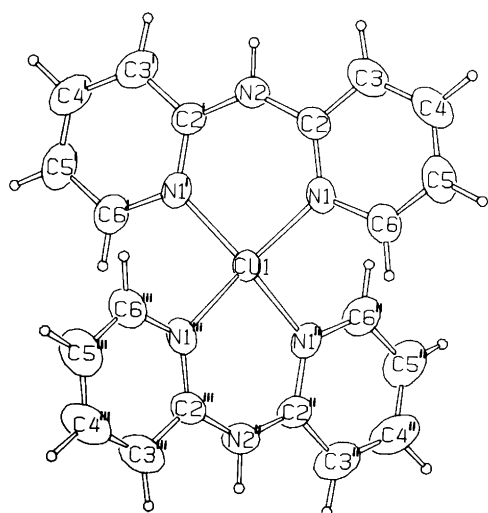


Fig. 1. The complex cation of compound 1. Thermal ellipsoids are plotted at the 50% probability level. Superscripts denote the following symmetry operations: ⁱ1 - x, 1 - y, z; ⁱⁱx, 1 - y, 1 - z; and ⁱⁱⁱ1 - x, y, 1 - z.

is four-coordinated, the CuN₄ chromophore having a compressed tetrahedral geometry, with a dihedral angle NCuN/NCuN (between the N-Cu-N planes of the two ligands) of 55.9(4)°. Cu-N bond distances are 1.957(2) Å, the N-Cu-N ligand bite angles are 94.1(1)°, and the other N-Cu-N angles are 99.4(2) and 139.9(2)°. Each dpa ligand is essentially planar, the torsion between its two pyridyl rings being 3°. The PF₆⁻ group is situated on a two-fold axis and shows a near regular octahedral geometry with P-F bond distances in the range

Table 5. Bond distances (in Å) and angles (in °) involving non-hydrogen atoms in compound 1, [CuL₂](PF₆)₂.

Atoms	Distance	Atoms	Distance
Cu1-N1	1.957(2)	C4-C5	1.319(4)
N1-C2	1.328(2)	C5-C6	1.362(3)
N1-C6	1.366(3)	P1-F1	1.579(2)
N2-C2	1.357(2)	P1-F2	1.554(2)
C2-C3	1.378(3)	P1-F3	1.569(2)
C3-C4	1.384(4)		
Atoms	Angle	Atoms	Angle
N1-Cu1-N1 ⁱⁱⁱ	139.9(2)	C4-C5-C6	120.1(2)
N1-Cu1-N1 ⁱⁱ	99.4(2)	N1-C6-C5	121.6(3)
N1-Cu1-N1 ⁱ	94.1(1)	F1-P1-F1 ⁱ	90.3(2)
Cu1-N1-C2	125.0(1)	F1-P1-F2	178.5(2)
Cu1-N1-C6	116.6(1)	F1-P1-F2 ⁱ	88.2(2)
C2-N1-C6	118.2(2)	F1-P1-F3	91.3(2)
C2-N2-C2 ⁱ	134.5(3)	F1-P1-F3 ⁱ	90.9(2)
N1-C2-N2	120.6(2)	F2-P1-F2 ⁱ	93.2(2)
N1-C2-C3	121.3(3)	F2-P1-F3	89.2(2)
N2-C2-C3	118.2(2)	F2-P1-F3 ⁱ	88.8(2)
C2-C3-C4	119.0(2)	F3-P1-F3 ⁱ	177.0(2)
C3-C4-C5	119.7(2)		

Superscripts refer to the following symmetry operations: ⁱ1 - x, 1 - y, z; ⁱⁱx, 1 - y, 1 - z; ⁱⁱⁱ1 - x, y, 1 - z.

Table 6. Bond distances (in Å) and angles (in °) involving non-hydrogen atoms in 2, [CuL₂(NO₃)₂].

Atom 1	Atom 2	Distance
Cu	O31	2.472(2)
Cu	N1A	2.016(2)
Cu	N1B	2.007(2)
O31	N3	1.246(3)
O32	N3	1.218(3)
O33	N3	1.244(3)
N1A	C2A	1.336(3)
N1A	C6A	1.354(3)
N1B	C2B	1.335(3)
N1B	C6B	1.361(3)
N2AB	C2A	1.378(3)
N2AB	C2B	1.376(3)
C2A	C3A	1.393(3)
C2B	C3B	1.400(3)
C3A	C4A	1.366(4)
C3B	C4B	1.346(4)
C4A	C5A	1.381(4)
C4B	C5B	1.380(4)
C5A	C6A	1.363(4)
C5B	C6B	1.356(4)

Atom 1	Atom 2	Atom 3	Angle
O31	Cu	N1A	85.26(7)
O31	Cu	N1B	96.83(6)
N1A	Cu	N1B	85.52(8)
Cu	O31	N3	129.4(1)
Cu	N1A	C2A	119.1(2)
Cu	N1A	C6A	121.7(2)
C2A	N1A	C6A	117.8(2)
Cu	N1B	C2B	120.5(1)
Cu	N1B	C6B	121.4(2)
C2B	N1B	C6B	117.6(2)
C2A	N2AB	C2B	126.1(2)
O31	N3	O32	120.4(2)
O31	N3	O33	120.3(2)
O32	N3	O33	119.3(2)
N1A	C2A	N2AB	119.5(2)
N1A	C2A	C3A	121.7(2)
N2AB	C2A	C3A	118.8(2)
N1B	C2B	N2AB	119.6(2)
N1B	C2B	C3B	121.4(2)
N2AB	C2B	C3B	118.9(2)
C2A	C3A	C4A	119.1(2)
C2B	C3B	C4B	119.3(2)
C3A	C4A	C5A	119.4(3)
C3B	C4B	C5B	119.5(2)
C4A	C5A	C6A	118.6(3)
C4B	C5B	C6B	118.5(2)
N1A	C6A	C5A	123.1(2)
N1B	C6B	C5B	123.4(2)

1.554–1.579 Å and F-P-F bond angles deviating less than 3° from 90 and 180°. The crystalline packing (Fig. 2) is such that contacts occur between the amine hydrogen H2 and two symmetry-related fluorine atoms of a PF₆⁻ group, H2-F1 = H2-F1ⁱ (1 - x, 1 - y, z) = 2.42 Å, the corresponding N2-F1 distances being 3.26 Å. These contacts may possibly represent a weak bifurcated hydrogen bond. Furthermore, four PF₆⁻ ions are pseudo-tetrahedrally arranged around each Cu ion, giving four

Table 7. Bond distances (in Å) and angles (in °) involving non-hydrogen atoms in compound 3, $[\text{CuL}_2(\text{NCS})_{1.5}\text{ClO}_4]_{0.5} \cdot [\text{CuL}_2(\text{NCS})]_2(\text{ClO}_4)_2$.

Atom 1	Atom 2	Distance
Cu1	N1A	2.015(4)
Cu1	N1B	2.022(3)
Cu1	N3	2.433(6)
Cu2	N1C	2.016(4)
Cu2	N1D	2.139(4)
Cu2	N1E	2.002(4)
Cu2	N1F	2.014(4)
Cu2	N4	1.996(4)
N1A	C2A	1.331(6)
N1A	C6A	1.366(6)
N1B	C2B	1.339(6)
N1B	C6B	1.359(6)
N1C	C2C	1.330(6)
N1C	C6C	1.355(6)
N1D	C2D	1.327(6)
N1D	C6D	1.362(7)
N1E	C2E	1.327(6)
N1E	C6E	1.351(6)
N1F	C2F	1.329(6)
N1F	C6F	1.368(6)
N2AB	C2A	1.379(6)
N2AB	C2B	1.382(6)
N2CD	C2C	1.387(6)
N2CD	C2D	1.395(6)
N2EF	C2E	1.397(6)
N2EF	C2F	1.384(6)
N3	C7	1.21(1)
N4	C8	1.142(7)
C2A	C3A	1.393(7)
C2B	C3B	1.403(6)
C2C	C3C	1.407(7)
C2D	C3D	1.396(7)
C2E	C3E	1.392(7)
C2F	C3F	1.402(7)
C3A	C4A	1.363(8)
C3B	C4B	1.350(7)
C3C	C4C	1.360(8)
C3D	C4D	1.390(8)
C3E	C4E	1.357(8)
C3F	C4F	1.357(8)
C4A	C5A	1.389(8)
C4B	C5B	1.388(8)
C4C	C5C	1.376(8)
C4D	C5D	1.37(1)
C4E	C5E	1.380(7)
C4F	C5F	1.384(8)
C5A	C6A	1.353(7)
C5B	C6B	1.359(7)
C5C	C6C	1.361(8)
C5D	C6D	1.355(8)
C5E	C6E	1.361(8)
C5F	C6F	1.357(7)
C7	S1	1.55(1)
C8	S2	1.633(5)
Cl1	O1	1.399(4)
Cl1	O2	1.435(5)
Cl1	O3	1.394(6)
Cl1	O4	1.378(7)
Cl2	O5	1.49(2)
Cl2	O6	1.37(3)
Cl2	O7	1.59(3)
Cl2	O8	1.20(2)
O8	Cu1	2.86(2)

Atom 1	Atom 2	Atom 3	Angle
N1A	Cu1	N1B	85.7(1)
N1A	Cu1	N3	86.9(2)
N1B	Cu1	N3	89.7(2)
N1C	Cu2	N1D	88.1(1)
N1C	Cu2	N1E	167.7(1)
N1C	Cu2	N1F	92.9(1)
N1C	Cu2	N4	86.1(2)
N1D	Cu2	N1E	103.8(1)
N1D	Cu2	N1F	101.1(1)
N1D	Cu2	N4	102.3(2)
N1E	Cu2	N1F	87.9(1)
N1E	Cu2	N4	88.3(2)
N1F	Cu2	N4	156.5(2)
O1	Cl1	O2	109.1(3)
O1	Cl1	O3	112.9(3)
O1	Cl1	O4	109.1(4)
O2	Cl1	O3	108.7(3)
O2	Cl1	O4	108.4(4)
O3	Cl1	O4	108.4(4)
O5	Cl2	O6	99(1)
O5	Cl2	O7	102(1)
O5	Cl2	O8	115(1)
O6	Cl2	O7	98(1)
O6	Cl2	O8	128(1)
O7	Cl2	O8	111(1)
C2C	N2CD	C2D	131.0(4)
C2E	N2EF	C2F	126.8(4)
N1A	C2A	N2AB	119.1(4)
N1A	C2A	C3A	122.2(4)
N2AB	C2A	C3A	118.6(4)
N1B	C2B	N2AB	119.6(4)
N1B	C2B	C3B	121.0(4)
N2AB	C2B	C3B	119.4(4)
N1C	C2C	N2CD	121.1(4)
N1C	C2C	C3C	121.6(4)
N2CD	C2C	C3C	117.3(4)
N1D	C2D	N2CD	120.0(4)
N1D	C2D	C3D	122.4(5)
N2CD	C2D	C3D	117.6(4)
N1E	C2E	N2EF	119.9(4)
N1E	C2E	C3E	121.7(4)
N2EF	C2E	C3E	118.5(4)
N1F	C2F	N2EF	119.5(4)
N1F	C2F	C3F	122.0(4)
N2EF	C2F	C3F	118.6(4)
C2A	C3A	C4A	118.6(4)
C2B	C3B	C4B	119.6(5)
C2C	C3C	C4C	118.5(4)
C2D	C3D	C4D	118.2(6)
C2E	C3E	C4E	119.0(4)
Cu1	N1A	C2A	120.7(3)
Cu1	N1A	C6A	121.0(3)
C2A	N1A	C6A	117.8(4)
Cu1	N1B	C2B	120.2(3)
Cu1	N1B	C6B	121.4(3)
C2B	N1B	C6B	117.9(4)
Cu2	N1C	C2C	122.1(3)
Cu2	N1C	C6C	116.8(3)
C2C	N1C	C6C	117.6(4)
Cu2	N1D	C2D	122.3(3)
Cu2	N1D	C6D	120.0(3)
C2D	N1D	C6D	117.6(4)
Cu2	N1E	C2E	122.6(3)
Cu2	N1E	C6E	118.3(3)
C2E	N1E	C6E	118.2(4)

Table continued

Table 7. Continued.

Atom 1	Atom 2	Atom 3	Angle
Cu2	N1F	C2F	123.5(3)
Cu2	N1F	C6F	118.8(3)
C2F	N1F	C6F	117.7(4)
C2A	N2AB	C2B	126.0(4)
Cu1	N3	C7	148.8(8)
Cu2	N4	C8	159.9(4)
Cu1	O8	Cl1	127(1)
C2F	C3F	C4F	119.1(5)
C3A	C4A	C5A	119.7(5)
C3B	C4B	C5B	119.9(4)
C3C	C4C	C5C	120.7(5)
C3D	C4D	C5D	119.4(5)
C3E	C4E	C5E	120.0(5)
C3F	C4F	C5F	119.4(5)
C4A	C5A	C6A	118.8(5)
C4B	C5B	C6B	118.0(5)
C4C	C5C	C6C	117.3(5)
C4D	C5D	C6D	119.0(6)
C4E	C5E	C6E	118.0(5)
C4F	C5F	C6F	119.0(5)
N1A	C6A	C5A	122.6(5)
N1B	C6B	C5B	123.4(4)
N1C	C6C	C5C	124.2(5)
N1D	C6D	C5D	123.3(5)
N1E	C6E	C5E	123.0(5)
N1F	C6F	C5F	122.7(4)
S1	C7	N3	166(1)
S2	C8	N4	179.5(5)

Cu...F2 distances of 3.67 Å. This is, however, too long to be considered even semi-coordination.¹⁹

Description of Structure 2. The crystal structure is composed of mononuclear, neutral [CuL₂(NO₃)₂] complex units (Fig. 3). The six-coordinated copper ion, situated at a centre of symmetry, is equatorially bonded to two bidentate dipyrindylamine ligands [Cu–N = 2.016(2) and 2.007(2) Å] and axially to monodentate nitrate groups [Cu–O₃₁ = 2.472(2) Å]. Each pyridyl ring is essentially planar (the maximum deviation from a mean plane is 0.038 Å), but the dihedral angle between the two aromatic rings within one ligand is 37.4°. The N–Cu–N bite angle is 85.5°. The monomeric units are connected through

nitrate–amine hydrogen bonds (Fig. 4), O33...N2AB ($x, \frac{1}{2} - y, z - \frac{1}{2}$) = 2.845(3) Å, ∠O...H–N = 166(2)°. The nitrate group shows a small deviation from trigonal symmetry, the N–O bonds involving coordinated and hydrogen-bonded oxygen atoms being slightly longer than the third bond, and the angles involving the coordinated oxygen atom being slightly larger than the third angle. The plane of the nitrate group makes an angle of 82.6° with the CuN₄ equatorial plane.

Description of structure 3. There are two crystallographically independent copper ions with totally different coordination geometries in the crystals. In molecule AB (Fig. 5a) Cu1 is six-coordinated, situated at a centre of symmetry, with two bidentate dipyrindylamine ligands in the equatorial plane [Cu1–N = 2.015(4) and 2.022(3) Å]. With a population of 0.75, the axial positions are occupied by the nitrogen atoms of SCN[−] groups, Cu–N = 2.433(6) Å. As discussed in the experimental section, perchlorate groups with an occupancy of 0.25 were fitted to the remaining electron density at the axial sites; this group is semi-coordinated to copper,¹⁹ Cu–O = 2.86(2) Å. In complex unit CF (Fig. 5b) Cu2 is five-coordinated, forming a Cu(dpa)₂(NCS)⁺ ion. The geometry may best be described as distorted square-pyramidal: there are two bidentate dipyrindylamine ligands; one of these bridges the apical and one of the equatorial positions, the isothiocyanato group occupies the last equatorial site [Cu–N(dpa, apical) = 2.139(4), Cu–N(dpa, equatorial) = 2.014(4), 2.016(4), 2.002(4) and Cu–NCS(equatorial) = 1.997(4)]. There is a slight distortion towards the trigonal bipyramidal geometry as revealed in the N–Cu–N angles (Table 7). The dihedral angle between the aromatic rings of a dipyrindylamine ligand in unit AB is 40.0°, and in unit CF it is 21.9 and 32.3°. The N–Cu–N bite angles are 85.7° in molecule AB and 88.1 and 87.9° in molecule CF.

In both the six- and five-coordinated complex units the isothiocyanate groups coordinate in a bent end-on configuration, the Cu–N–C angles being 148.8 (molecule AB) and 159.9° (molecule CF). The three crystallographically independent amine groups are all involved in interactions that may be considered intermediate to weak

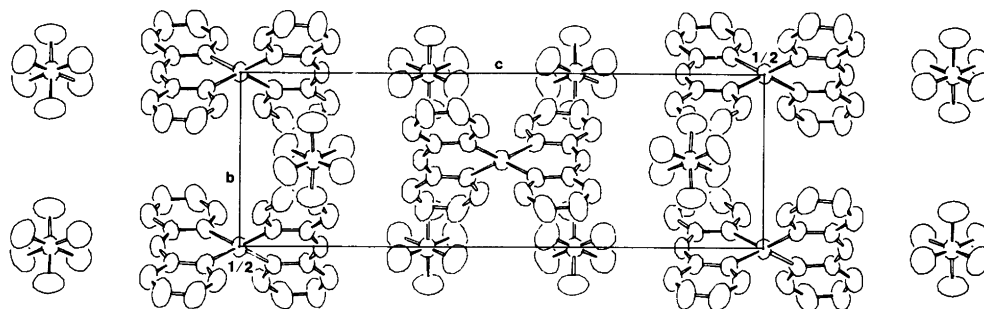


Fig. 2. Crystalline packing in compound 1 as viewed down the *a*-axis. The origin is in the upper left-hand corner with *c* running horizontally (0–1/2) and *b* vertically (0–1/2).

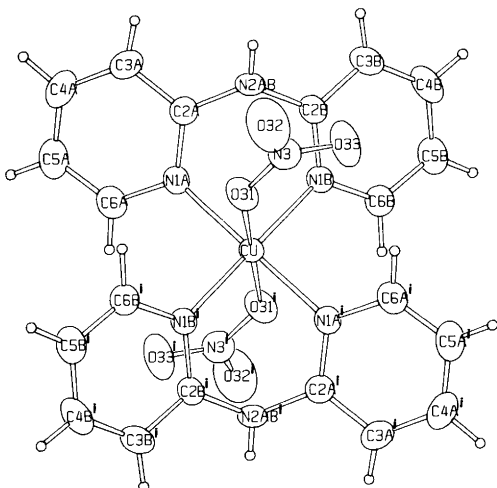


Fig. 3. The complex unit of compound **2**. Thermal ellipsoids are plotted at the 50% probability level. Superscript ⁱ denotes the symmetry operation $-x, 1-y, -z$.

hydrogen bonds. N2AB interacts with the uncoordinated perchlorate ion, $\text{N2AB} \cdots \text{O1}(x, y, z) = 3.057(6) \text{ \AA}$, $\angle \text{N2AB-H} \cdots \text{O1} = 154^\circ$; N2CD with the disordered, semi-coordinated perchlorate ion, $\text{N2CD} \cdots \text{O5}(1-x, -y, 1-z) = 2.79(2) \text{ \AA}$, $\angle \text{N2CD-H} \cdots \text{O5} = 177^\circ$ or weakly with the corresponding isothiocyanate ion, $\text{N2CD} \cdots \text{S1}(1-x, -y, 1-z) = 3.465(5) \text{ \AA}$, $\text{N2CD-H} \cdots \text{S1} = 144^\circ$; N2EF interacts weakly with the isothiocyanate in a neighbouring five-coordinated complex ion, $\text{N2EF} \cdots \text{S2}(1-x, -y, 1-z) = 3.455(4) \text{ \AA}$, $\angle \text{N2EF-H} \cdots \text{S2} = 136^\circ$.

Discussion

Coordination geometries in bis(dpa)copper(II) complexes.

Four-, five- and six-coordination have been observed in these complexes, depending on counter ion and crystal packing effects.

The compressed tetrahedral CuN_4 chromophore observed in **1**, $[\text{Cu}(\text{dpa})_2](\text{PF}_6)_2$, is identical to that of the analogous perchlorate,⁵ within experimental error. This coordination geometry allows the pyridyl rings within one dpa ligand to be almost coplanar, and gives an N–Cu–N bite angle of close to 95° . The neutral copper(II) complex obtained with the deprotonated di-2-pyridylamide ligand, $\text{Cu}(\text{dpa-H})_2$, has essentially the same geometry ($\text{NCuN}/\text{NCuN} = 58.8^\circ$).²⁰ The closely related compound $\text{Cu}(\text{bpy})_2(\text{PF}_6)_2$ also features the compressed tetrahedral CuN_4 chromophore,²¹ although with an appreciably smaller NCuN/NCuN dihedral angle (44.6°) and N–Cu–N bite angle (83.0°). It may be noticed at this point that in $[\text{Cu}(\text{bpy})_2\text{X}]\text{X}$, X being ClO_4^- and BF_4^- , tetrahedral CuN_4 chromophores with dihedral angles 44.6 and 44.7° are also found, although in these cases anions serve as bridging ligands semi-coordinated in axial positions in six-coordinated complexes.²² The Cu–N bond lengths are short in all the compressed tetrahedral $\text{Cu}(\text{II})(\text{dpa})_2^{2+}$ and $\text{Cu}(\text{II})(\text{dpa-H})_2$ complexes, with an average of $1.955(14) \text{ \AA}$; in the corresponding $\text{Cu}(\text{II})(\text{bpy})_2^{2+}$ complexes the distance is $1.989(14) \text{ \AA}$. These observations demonstrate a noticeable difference between the chelate functions of bpy and the more flexible dpa ligand.

The elongated centrosymmetric octahedral geometry found in **2** and in molecule AB of compound **3**, has also been observed in the $[\text{Cu}(\text{dpa})_2]\text{X}_2$ (X = *O*-tricyanoethyleneoate) complex unit.⁶ The equatorial Cu–N distances in these complexes range from 1.989 to 2.022 \AA with an average of $2.011(12) \text{ \AA}$, and are thus significantly longer than in the compressed tetrahedral geometry. The planar, equatorial coordination of the four pyridyl nitrogen atoms is only possible because of the flexibility of the dipyridylamine groups which in these three complexes are puckered such that the angles between the planes of pyridyl rings within one ligand are 37.4 , 40.0 and 41.4° , respectively. The N–Cu–N bite angles are 85.5 , 85.7

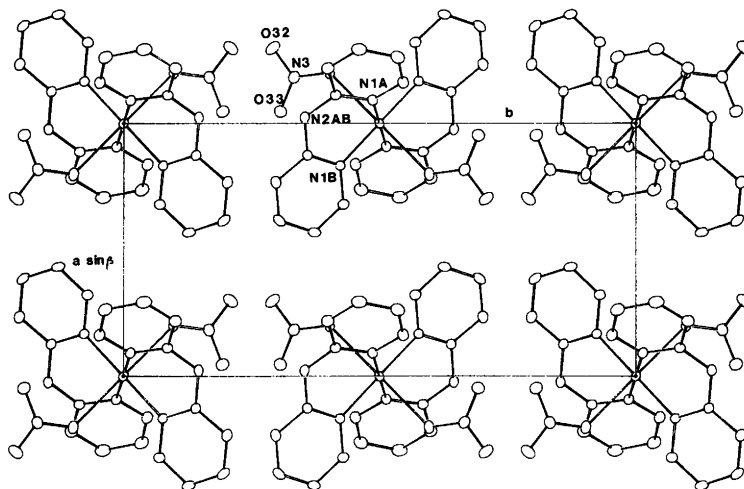


Fig. 4. Crystalline packing in compound **2** as viewed down the *c*-axis. The origin is in the upper left-hand corner with *b* running horizontally and *a* vertically.

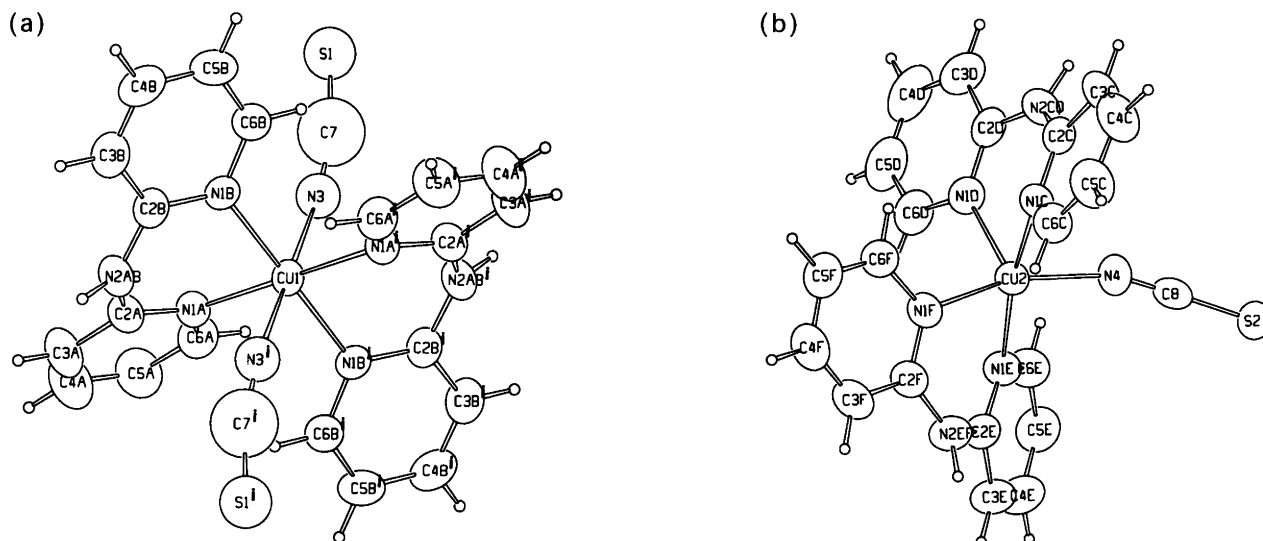


Fig. 5. (a) Complex unit AB in compound **3**. Only the isothiocyanato group which coordinates in the axial positions with an occupancy of 0.75 is drawn. Superscript ⁱ denotes the symmetry operation $-x, -y, -z$. (b) Complex unit CF in compound **3**. Thermal ellipsoids are plotted at the 50% probability level.

and 86.3° , appreciably smaller than in the compressed tetrahedral complexes. An analogous coordination geometry has not been found in complexes with the less flexible bpy ligand. Complexes $[\text{Cu}(\text{bpy})_2(\text{ClO}_4)](\text{ClO}_4)$ and $[\text{Cu}(\text{bpy})_2(\text{BF}_4)](\text{BF}_4)$,²² although six-coordinated, are not centrosymmetric and have a strong tetrahedral distortion, as mentioned above. The complex unit in $\text{Cu}(\text{bpy})_2(\text{NO}_3)_2$ is totally different from that in **2**, featuring a geometry best described as *cis*-distorted octahedral with a marked asymmetric, bidentate coordination of one of the nitrate groups.²³ Two bis(dpa)copper(II) complexes with acetate and formate as anions show the same type of distortion.¹¹ This geometry is more closely related to the five-coordinated complexes discussed below than to an elongated octahedral geometry.

In the five-coordinated molecule CF of **3** the coordination geometry is square-based pyramidal with a small

trigonal distortion, one of the dpa ligands bridging the axial and one of the equatorial positions. The τ -value defined to describe the degree of trigonal distortion²⁴ is 0.18 for this compound, and is the lowest value found in the five-coordinated bis(dpa)copper(II) complexes known to date. Most close in geometry are the chromophores of $[\text{Cu}(\text{dpa})_2\text{Cl}]\text{Cl} \cdot 4\text{H}_2\text{O}$ ($\tau = 0.25$),⁸ and $[\text{Cu}(\text{dpa})_2(\text{NCO})_2](\text{SO}_4)(\text{dpa})_2 \cdot \text{H}_2\text{O}$ ($\tau = 0.30$).¹⁰ In the corresponding compounds $[\text{Cu}(\text{dpa})_2\text{Cl}]\text{Cl}$ (Ref. 9) and $[\text{Cu}(\text{dpa})_2\text{I}]_2\text{I}(\text{ClO}_4)$ (Ref. 7) the distortion towards trigonal bipyramidal geometry is considerably more pronounced, τ -values of 0.57, 0.63 and 0.65 are found. There is a substantial number of five-coordinated $[\text{Cu}(\text{bpy})_2\text{X}]^+$ complexes with coordination geometries intermediate between square pyramidal and trigonal bipyramidal. Several of these bipyridyl complexes have very close to trigonal bipyramidal geometry, e.g.

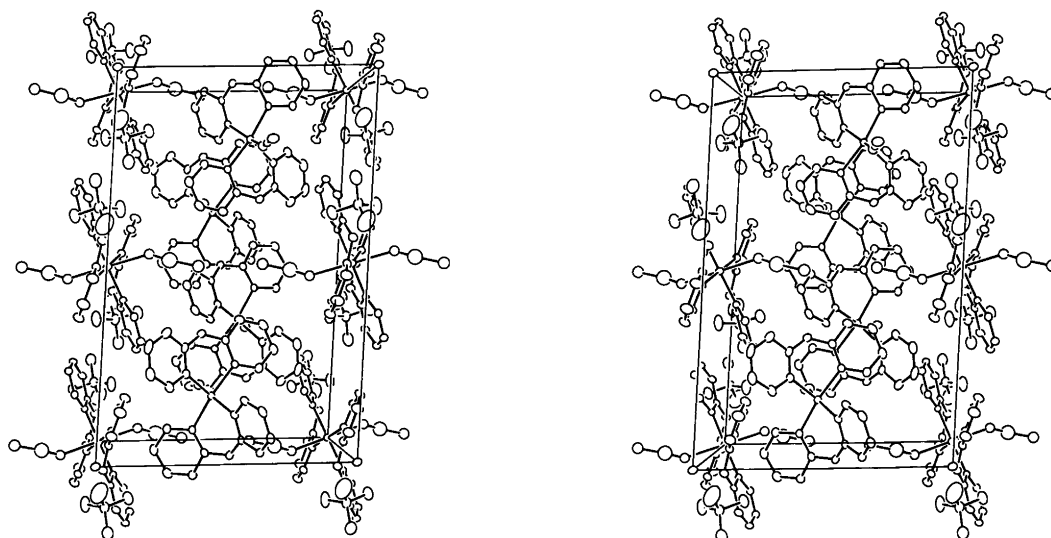


Fig. 6. Crystalline packing in compound **3** as viewed down the *b*-axis. The origin is in the upper left-hand corner with *a* running horizontally and *c* vertically.

[Cu(bpy)₂(NCS)](NO₃)₃ ($\tau = 0.89$), [Cu(bpy)₂Cl]Cl · 6H₂O ($\tau = 0.93$)²⁵ and [Cu(bpy)₂I](ClO₄) ($\tau = 0.86$).²⁶ Some cases with τ -values around 0.6 are known, e.g. one of the molecules in [Cu(bpy)₂(NCS)](NCS) ($\tau = 0.65$)²⁷ and [Cu(bpy)₂(NCS)](BF₄) ($\tau = 0.61$).²⁸ Only a few cases close to square pyramidal geometry are found, e.g. for one of the Cu atoms in each of the dimers [(Cu(bpy)₂)₂(OH)](ClO₄)₃ ($\tau = 0.32$)²⁹ and [(Cu(bpy)₂)₂(NO₃)](PF₆)₃ ($\tau = 0.04$).⁴ It is to be noted, however, that in both of these cases the square-based pyramid is tetrahedrally distorted rather than trigonally, and also in the latter example the nitrate bridge coordinates in an apical position. In other cases where the τ -value indicates a geometry close to square pyramidal, a sixth atom is semi-coordinated, as in [Cu(bpy)₂(O₂CMe)](BF₄) for example ($\tau = 0.36$),³⁰ and the geometry is rather *cis*-distorted octahedral. It thus appears that the near-regular square-based pyramidal geometry may be better attained with di-2-pyridylamine as ligands.

Geometry of di-2-pyridylamine ligands. The near coplanarity of the aromatic rings within a dpa molecule in the tetrahedrally compressed complexes is associated with a wide C–N–C angle at the amine nitrogen, 134.5 and 134° in compound **1** and the corresponding perchlorate,⁵ respectively. With increasing pyridyl/pyridyl dihedral angle the C–N–C angle decreases; in the three centrosymmetric octahedrally elongated complexes known, with dihedral angles in the range 37.4–41.4°, C–N–C angles in the range 125.1–126.1° are found [compounds **2**, **3**(AB) and Ref. 6]. In the five-coordinated Cu(dpa)₂X complexes [compound **3**(CF) and Refs. 7–10], where the angle between pyridyl rings ranges from 18.2 to 40°, the spread in C–N–C angles observed is 121.3–131.0°. An increased puckering of the ligand also leads to a slight increase in C–N(amine) bond distances; in **1** this distance is 1.357(2) Å, while in the six-coordinated species mentioned above the corresponding average distance is 1.380(4) Å. The N—N bite of the ligand with near-coplanar pyridyl rings in the compressed tetrahedral complex **1** is 2.865 Å, while it is approximately 2.74 Å in the six-coordinated complexes, and ranges from 2.73 to 2.89 Å in the five-coordinated complexes.

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