

The Plasticity of Cu(II) in [Cu(bipyridyl)₂X]ⁿ⁺ Chromophores. Crystal and Molecular Structure of Tetrakis(2,2'-bipyridyl)-μ-nitratodicopper(II) Hexafluorophosphate

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The structure of the title compound, denoted [(Cu(bpy)₂)₂(NO₃)](PF₆)₃, has been determined by X-ray crystallographic methods using data collected at 294 K on a CAD4 diffractometer. The crystals are triclinic, space group *P*1, with cell dimensions *a* = 11.930(6), *b* = 14.235(4), *c* = 14.995(5) Å, α = 85.68(2), β = 68.95(3), γ = 76.70(3)°. The structure was solved by direct methods and successive Fourier syntheses. Full-matrix least-squares refinement converged at an *R* value of 0.094. The compound consists of binuclear [(Cu(bpy)₂)₂(NO₃)]³⁺ entities and non-coordinated PF₆⁻ counter-ions. The two crystallographically independent copper atoms are asymmetrically bridged by the nitrate group and have totally different coordination geometries. The nitrate binds to CuA in a marked asymmetric, bidentate fashion, giving a (4 + 1 + 1*) asymmetric *cis*-distorted octahedral structure. CuB has a square-pyramidal geometry with a pronounced tetrahedral distortion, the nitrate binding monodentately at the axial position.

Copper(II) complexes are known to display a large variation of non-regular stereochemistries.¹ The coordination geometry may e.g. vary appreciably for the same set of ligands in different crystal environments. To describe this property of the Cu(II) ion, the term “plasticity” has been introduced.² A number of complexes of composition [Cu(bpy)₂X]Y have been studied, and Cu coordination geometries ranging from almost regular trigonal bipyramidal to compressed tetrahedral and bicapped square-pyramidal have been observed. The results from this series of closely related compounds have been used to define structural pathways between different coordination geometries.³

The present work reports the crystal structure of a new member of this group of complexes, in which two nitrate-bridged copper atoms have totally different and unusual CuN₄O chromophore stereochemistries.

Experimental

The compound was obtained as a side-product in a synthesis aimed at producing a dinuclear copper complex with an oxamido derivative as bridging ligand. A method analogous to those described by Nonoyama *et al.* was used.⁴ Dark blue, polyhedral crystals were obtained by slow evaporation from ethanol solution.

Crystallographic data are summarized in Table 1. Cell dimensions were determined by least-squares refinement of 2θ values from 25 reflections (15 < 2θ < 21°) accurately

Table 1. Information concerning the crystallographic data collection and refinement conditions for [(Cu(bpy)₂)₂(NO₃)](PF₆)₃.

Molecular formula	Cu ₂ C ₄₀ F ₁₈ H ₃₂ N ₉ O ₃ P ₃
Formula weight	1248.73
Space group	<i>P</i> 1 (No. 2)
Temperature/°C	21
Unit cell <i>a</i> /Å	11.918(6)
<i>b</i> /Å	14.250(4)
<i>c</i> /Å	15.013(5)
α/°	85.51(2)
β/°	68.81(2)
γ/°	76.67(2)
<i>V</i> /Å ³	2313(2)
<i>Z</i>	2
<i>D_x</i> /g cm ⁻³	1.793
μ/cm ⁻¹	11.438
Range of absorption correction factors	1.74–1.03
Crystal size/mm	0.295 × 0.301 × 0.083
Instrument	CAD-4
Scan type	ω
Scan range, Δω/°	1.1 + 0.34 tan Θ
Scan speed/° min ⁻¹	2.3
Radiation	Mo Kα (λ = 0.710 73 Å)
Max 2θ/°	52
No. of reflections measured	9080
No. of “observed” reflections, NO	4081
Limit of “observed” reflections	<i>F_o</i> > 3σ
No. variables refined, NV	676
<i>R</i> ^a	0.094
<i>R_w</i> ^a	0.085
<i>s</i> ^a	3.38

^aAgreement factors are defined as follows:

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $s = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$. The weighting scheme is defined by: $w = 1/\sigma_F^2$; $\sigma_F = \sigma_1 (|Lp|)^{-1/2}$; $\sigma_1 = [\sigma_c^2 + (0.02N_{\text{net}})^2]^{1/2}$.

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Table 2. Positional parameters and equivalent isotropic temperature factors for non-hydrogen atoms. $B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

Atom	x	y	z	$B_{eq}/\text{\AA}^2$	Atom	x	y	z	$B_{eq}/\text{\AA}^2$
CuA	0.1688(1)	0.4737(1)	0.72229(9)	3.21(4)	C4A	0.176(1)	0.4255(8)	0.4507(8)	3.3(3)
CuB	0.3350(1)	0.0425(1)	0.78767(9)	3.13(4)	C5A	0.190(1)	0.4622(9)	0.5295(7)	2.9(3)
PA	-0.0012(3)	0.8354(3)	0.6772(2)	4.4(1)	C6A	0.271(1)	0.5206(8)	0.5244(7)	2.6(3)
PB	0.5046(3)	-0.2500(3)	0.7517(2)	4.1(1)	C7A	0.336(1)	0.567(1)	0.4450(8)	4.1(4)
PC	0.7197(4)	0.2784(3)	0.7897(3)	4.8(1)	C8A	0.407(1)	0.624(1)	0.4480(9)	4.8(4)
F1A	0.1345(6)	0.8411(6)	0.6642(5)	6.6(2)	C9A	0.419(1)	0.641(1)	0.5362(9)	5.3(4)
F2A	-0.0259(9)	0.7946(7)	0.7797(5)	9.0(3)	C10A	0.351(1)	0.5937(9)	0.6141(8)	4.2(4)
F3A	0.042(1)	0.7294(8)	0.6357(7)	12.7(4)	C11A	0.345(1)	0.475(1)	0.8177(8)	4.1(4)
F4A	-0.048(1)	0.9378(6)	0.7237(7)	9.7(4)	C12A	0.387(1)	0.501(1)	0.8835(9)	5.8(5)
F5A	-0.1351(7)	0.8295(8)	0.6886(6)	9.5(3)	C13A	0.302(1)	0.561(1)	0.9593(9)	5.4(4)
F6A	0.0192(8)	0.881(1)	0.5768(6)	12.1(4)	C14A	0.181(1)	0.5900(9)	0.9641(8)	4.7(4)
F1B	0.6321(8)	-0.2262(9)	0.7156(7)	12.1(4)	C15A	0.146(1)	0.5629(8)	0.8932(7)	3.5(3)
F2B	0.4589(9)	-0.178(1)	0.8324(7)	17.2(4)	C16A	0.022(1)	0.5856(8)	0.8921(8)	3.4(3)
F3B	0.451(1)	-0.167(1)	0.6975(8)	17.2(5)	C17A	-0.075(1)	0.6399(9)	0.9653(9)	5.0(4)
F4B	0.552(1)	-0.3282(9)	0.804(1)	25.1(5)	C18A	-0.192(2)	0.657(1)	0.9634(9)	6.6(5)
F5B	0.3760(7)	-0.2744(7)	0.7858(7)	8.6(3)	C19A	-0.211(1)	0.628(1)	0.887(1)	7.2(5)
F6B	0.5479(9)	-0.3121(9)	0.6660(8)	22.9(4)	C20A	-0.113(1)	0.573(1)	0.8143(9)	5.3(4)
F1C	0.7159(7)	0.1684(6)	0.8110(5)	7.0(2)	C1B	0.158(1)	0.074(1)	0.6825(8)	4.1(4)
F2C	0.7933(9)	0.2552(8)	0.6800(6)	9.8(4)	C2B	0.122(1)	0.105(1)	0.6059(9)	5.4(4)
F3C	0.8436(8)	0.2665(8)	0.8098(6)	11.2(3)	C3B	0.204(1)	0.1332(9)	0.5246(8)	4.6(4)
F4C	0.5974(7)	0.2904(7)	0.7678(6)	8.1(3)	C4B	0.322(1)	0.1318(8)	0.5210(7)	4.1(4)
F5C	0.7235(9)	0.3896(6)	0.7686(6)	8.8(3)	C5B	0.356(1)	0.0985(8)	0.5993(7)	3.0(3)
F6C	0.645(1)	0.3019(8)	0.8963(6)	11.4(4)	C6B	0.478(1)	0.0926(8)	0.6034(7)	3.0(3)
O1A	0.1209(7)	0.3507(5)	0.8029(5)	3.6(2)	C7B	0.574(1)	0.1131(9)	0.5279(8)	4.2(4)
O1B	0.1976(9)	0.2057(6)	0.8367(5)	5.2(3)	C8B	0.687(1)	0.106(1)	0.5393(9)	5.6(5)
O2	0.3075(9)	0.2874(7)	0.7237(6)	5.9(3)	C9B	0.700(1)	0.064(1)	0.6210(9)	4.6(4)
N1A	0.1204(8)	0.4325(7)	0.6186(6)	3.2(3)	C10B	0.602(1)	0.0427(9)	0.6927(8)	3.6(3)
N2A	0.2785(8)	0.5372(6)	0.6125(6)	3.0(2)	C11B	0.440(1)	0.1210(8)	0.9105(8)	3.0(3)
N3A	0.2323(9)	0.5040(7)	0.8198(6)	3.5(3)	C12B	0.441(1)	0.1495(8)	0.9977(8)	3.2(3)
N4A	0.0049(9)	0.5572(7)	0.8189(6)	3.1(3)	C13B	0.364(1)	0.1117(9)	1.0802(8)	3.5(3)
N1B	0.2693(8)	0.0718(7)	0.6787(6)	3.2(3)	C14B	0.287(1)	0.0564(9)	1.0736(7)	3.4(3)
N2B	0.4880(8)	0.0580(7)	0.6881(6)	3.0(3)	C15B	0.2905(9)	0.0306(8)	0.9851(7)	2.1(3)
N3B	0.3678(8)	0.0686(7)	0.9058(6)	2.8(2)	C16B	0.215(1)	-0.0251(8)	0.9691(7)	2.4(3)
N4B	0.2218(8)	-0.0311(7)	0.8777(5)	2.8(2)	C17B	0.146(1)	-0.0806(8)	1.0399(8)	3.0(3)
N5	0.2088(9)	0.2799(7)	0.7882(6)	3.9(3)	C18B	0.079(1)	-0.1341(9)	1.0195(8)	4.0(4)
C1A	0.040(1)	0.3831(9)	0.6288(8)	3.8(3)	C19B	0.087(1)	-0.1435(8)	0.9263(8)	3.5(3)
C2A	0.018(1)	0.3484(9)	0.5525(9)	4.2(4)	C20B	0.160(1)	-0.0882(8)	0.8596(7)	2.8(3)
C3A	0.092(1)	0.373(1)	0.4620(8)	4.2(4)					

centred on the diffractometer. During intensity data collection a decay of approximately 30% occurred in the intensity of one of the reference reflections, while the other two references decreased by 8 and 4% only; the data were scaled in accordance with the average decay. An empirical method of absorption correction was used, after isotropic refinement.⁵ The structure was solved by direct methods and successive Fourier syntheses, and refined by full-matrix least-squares refinement. The process of locating all non-hydrogen atoms and refining the partial structure was slow and difficult. This was probably caused by the presence of pseudo-*I*-centring in the crystal; two crystallographically independent copper atoms are separated by approximately 1/2, 1/2, 1/2. The pseudo-centring of the cell leads to an unusually high ratio of "unobserved" reflections (Table 1). All non-hydrogen atoms were refined anisotropically. Hy-

drogen atoms could not be located; they were included at calculated positions (C-H = 0.95 Å) but were not refined. The refinement converged at an *R* value of 0.094. The relatively poor agreement factor may be related to the anisotropic crystal deterioration during data collection. The scattering factors, with anomalous dispersion terms included, were those of Cromer and Waber.⁶ All calculations were carried out on a MICRO-VAXII computer using the Enraf-Nonius structure determination programs.⁷

Results and discussion

Atomic coordinates and isotropic equivalent thermal parameters of non-hydrogen atoms are listed in Table 2. Selected bond distances and angles are listed in Tables 3 and 4. Lists of anisotropic thermal parameters, hydrogen

Table 3. Bond distances (in Å) involving non-hydrogen atoms in the cation, $[(\text{Cu}(\text{bpy})_2)_2(\text{NO}_3)]^{3+}$.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
CuA	O1A	2.120(5)	C4A	C5A	1.408(9)
CuA	O2	2.788(6)	C5A	C6A	1.391(9)
CuA	N1A	2.012(5)	C6A	C7A	1.377(9)
CuA	N2A	2.000(6)	C7A	C8A	1.31(1)
CuA	N3A	1.988(6)	C8A	C9A	1.43(1)
CuA	N4A	2.118(6)	C9A	C10A	1.39(1)
CuB	O1B	2.505(5)	C11A	C12A	1.37(1)
CuB	N1B	2.033(5)	C12A	C13A	1.41(1)
CuB	N2B	1.942(6)	C13A	C14A	1.39(1)
CuB	N3B	2.027(5)	C14A	C15A	1.38(1)
CuB	N4B	1.965(6)	C15A	C16A	1.44(1)
O1A	N5	1.243(7)	C16A	C17A	1.40(1)
O1B	N5	1.240(8)	C17A	C18A	1.37(1)
O2	N5	1.247(8)	C18A	C19A	1.36(1)
N1A	C1A	1.279(9)	C19A	C20A	1.41(1)
N1A	C5A	1.390(8)	C1B	C2B	1.38(1)
N2A	C6A	1.397(8)	C2B	C3B	1.36(1)
N2A	C10A	1.31(1)	C3B	C4B	1.38(1)
N3A	C11A	1.298(9)	C4B	C5B	1.390(9)
N3A	C15A	1.381(8)	C5B	C6B	1.46(1)
N4A	C16A	1.299(8)	C6B	C7B	1.36(1)
N4A	C20A	1.39(1)	C7B	C8B	1.39(1)
N1B	C1B	1.300(9)	C8B	C9B	1.37(1)
N1B	C5B	1.358(8)	C9B	C10B	1.35(1)
N2B	C6B	1.366(8)	C11B	C12B	1.407(9)
N2B	C10B	1.350(9)	C12B	C13B	1.40(1)
N3B	C11B	1.280(8)	C13B	C14B	1.37(1)
N3B	C15B	1.377(8)	C14B	C15B	1.391(8)
N4B	C16B	1.353(7)	C15B	C16B	1.418(9)
N4B	C20B	1.317(9)	C16B	C17B	1.404(9)
C1A	C2A	1.40(1)	C17B	C18B	1.35(1)
C2A	C3A	1.40(1)	C18B	C19B	1.381(9)
C3A	C4A	1.34(1)	C19B	C20B	1.393(9)

parameters, structure amplitudes, all bond distances and angles, as well as least-squares planes, are available on request from one of the authors (J.S.).

Each asymmetric unit consists of a dinuclear cation in which the copper atoms are asymmetrically bridged by a nitrate group (Fig. 1), and three uncoordinated PF_6^- counter-ions in the crystal lattice (Fig. 2). The two crystallographically independent Cu(II) atoms have distinctly different coordination geometries.

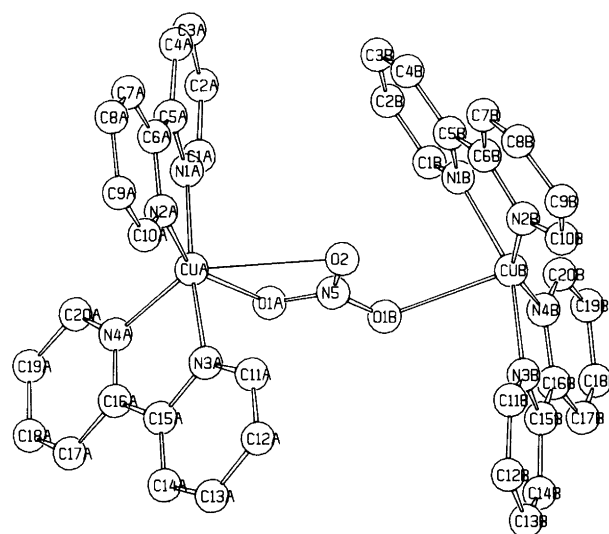


Fig. 1. The dinuclear cation, $[(\text{Cu}(\text{bpy})_2)_2(\text{NO}_3)]^{3+}$. The bond between CuA and the semi-coordinated O2 atom is indicated with a single line.

The $[\text{Cu}(\text{bpy})_2\text{X}]^{n+}$ chromophores. In an isolated Cu(II) A_5 polyhedron with A equal and unidentate ligands, the apically elongated square pyramidal coordination geometry is energetically favoured with respect to the compressed trigonal bipyramidal.⁸ The energy difference between the two geometries is small, however, and geometric ligand and/or counter-ion effects may well change the relative stabilities. Indeed the regular square pyramidal and trigonal bipyramidal geometries are only rarely found in five-coordinated Cu(II) complexes.¹ In $[\text{Cu}(\text{bpy})_2\text{X}]^{n+}$ systems, with X being monodentate ligands, various degrees of distortions from the trigonal bipyramidal geometry have been observed.⁹⁻¹⁷ The structural parameters most suitable for characterizing the distortion from a regular trigonal bipyramidal geometry are the angles α_1 – α_5 as shown in Fig. 3.¹⁷ In these systems, four ligand atoms are equivalent, and structural pathways for distortion from a trigonal bipyramidal towards a square pyramidal geometry may occur along two alternative routes: route A, where α_3 increases and Cu– X is lengthened, or route B, where α_1 is increased and Cu–N4 is lengthened.^{10,17}

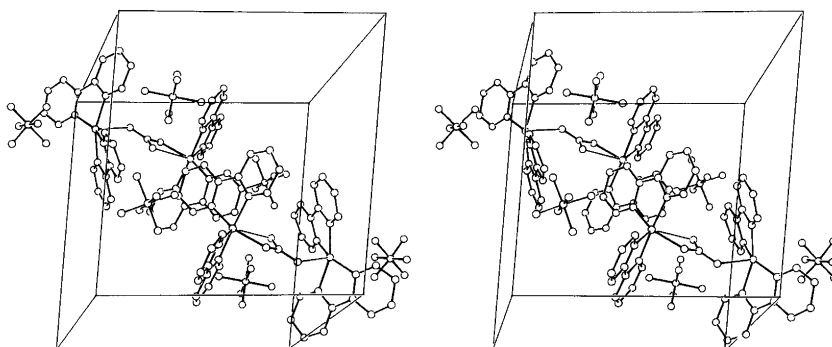


Fig. 2. Stereoscopic view down the a^* axis. The origin is in the lower left-hand corner with b running horizontally.

Table 4. Bond angles (in °) at copper atoms.

Atom 1	Atom 2	Atom 3	Angle
O1A	CuA	O2	49.0(2)
O1A	CuA	N1A	89.8(2)
O1A	CuA	N2A	152.3(2)
O1A	CuA	N3A	88.8(2)
O1A	CuA	N4A	87.7(2)
O2	CuA	N1A	89.1(2)
O2	CuA	N2A	104.1(2)
O2	CuA	N3A	85.7(2)
O2	CuA	N4A	134.8(2)
N1A	CuA	N2A	82.0(3)
N1A	CuA	N3A	174.2(3)
N1A	CuA	N4A	105.5(3)
N2A	CuA	N3A	96.6(2)
N2A	CuA	N4A	120.0(2)
N3A	CuA	N4A	80.2(3)
O1B	CuB	N1B	79.2(2)
O1B	CuB	N2B	108.8(2)
O1B	CuB	N3B	78.7(2)
O1B	CuB	N4B	96.2(2)
N1B	CuB	N2B	82.5(3)
N1B	CuB	N3B	157.4(2)
N1B	CuB	N4B	103.6(3)
N2B	CuB	N3B	100.8(3)
N2B	CuB	N4B	154.9(2)
N3B	CuB	N4B	82.9(2)

In the CuN_4O chromophore of CuA the α_1 – α_5 angles are 152, 88, 120, 90 and 89°, respectively, while CuA–N1A and CuA–O1A are both 2.12 Å. This suggests that the distortion from trigonal bipyramidal towards square pyramidal geometry is best described as a superposition of

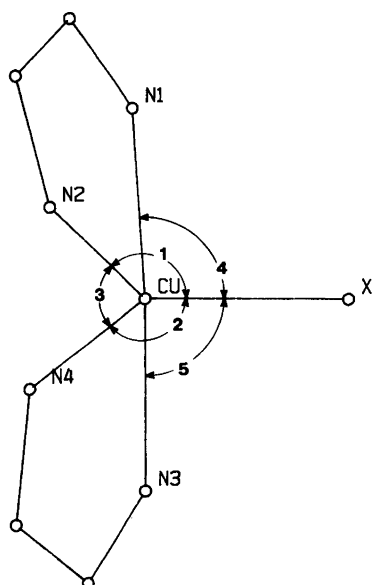


Fig. 3. Angles, numbered α_1 to α_5 , referred to in characterizing the distortion from regular trigonal bipyramidal geometry in $[\text{Cu}(\text{bpy})_2\text{X}]^{n+}$ systems.

deformation along routes A and B, with route B as the major component. However, while the stereochemistry is basically five-coordinate, a complete description of the coordination geometry has to include oxygen atom O2 of the nitrate group. Situated at 2.79 Å from CuA, it may be classified as semi-coordinated to copper.¹⁸ The situation is similar in several other $[\text{Cu}(\text{bpy})_2\text{X}]^{n+}$ systems where X is a potentially bidentate ligand.^{19–25} The first such structure to be studied was $[\text{Cu}(\text{bpy})_2(\text{NO}_2)](\text{NO}_3)$.²¹ In the room-temperature X-ray investigation a regular *cis*-distorted octahedral coordination geometry was found, with one nitrogen atom from each bipyridyl group as axial ligand atoms and both nitrite oxygen atoms equatorial and at equal distances from Cu. From later analyses of a number of related systems, as well as low-temperature studies of the nitrite compound mentioned above, it has been concluded that the *cis*-distorted octahedral geometry is not a genuine static stereochemistry of Cu(II) complexes, but appears as an artefact owing to the fluxional behaviour of the Cu(II) ion.^{22b,c} The static structures found have been classified by Hathaway based on the types of distortions from the regular *cis*-distorted geometry.³ Following this classification, CuA may be described as having an asymmetric *cis*-distorted octahedral 4 + 1 + 1* geometry. The in-plane Cu–N distances (CuA–N2 and CuA–N4) differ by $\Delta N = 0.118$ Å and the Cu–O distances by $\Delta O = 0.669$ Å. For a series of complexes exhibiting this type of 4 + 1 + 1* distortion geometry a correlation between increasing ΔN and ΔO values, for Cu–O2 up to approximately 2.8 Å, has been noticed.^{19,24} The values in the present investigation fit nicely into this scheme, which suggests that O2 has an influence even at a distance of close to 2.8 Å. When compared with the other 4 + 1 + 1* distorted complexes mentioned above,^{19–25} the present chromophore is special in having an α_2 angle of less than 90°. Also, the α_3 angle of 120° is unusually wide; in the other complexes with significant Cu–N4 lengthening, this angle has been found in the range 96–113°. Only in the nitrate complex previously studied²⁰ is an α_3 angle larger than 120° observed, but this chromophore differs from the present one in having a long Cu–O1 bond of 2.30 Å; i.e. when considering CuN_4O , the distortion from trigonal bipyramidal geometry is solely along route A.

In the CuN_4O chromophore of CuB α_1 , α_2 and α_3 are 109, 96 and 155°, respectively, and CuB–O1B is a rather weak bond [2.51 Å]. The O2 atoms is too far removed from copper [3.52 Å] to be considered even semi-coordinated. Clearly the geometry is closer to square pyramidal than to trigonal bipyramidal; a large distortion from trigonal bipyramidal along route A, as explained above, might be envisaged. However, as atoms N1B to N4B deviate by –0.41, +0.41, –0.41 and +0.41 Å, respectively, from a best equatorial plane for CuB, and with Cu1B only –0.014 Å from this plane, it is clear that there is an appreciable tetrahedral distortion superposed on the type-A distortion. In accordance with this, α_4 and α_5 are both acute, 79°. In most other $[\text{Cu}(\text{bpy})_2\text{X}]^{n+}$

systems these angles are larger than 90° , but tetrahedral distortions do occur in a few such complexes; e.g. in $[\text{Cu}(\text{bpy})_2(\text{H}_2\text{O})](\text{S}_2\text{O}_4)$,¹⁵ $[\text{Cu}(\text{bpy})_2(\text{S}_2\text{O}_8)](\text{H}_2\text{O})$,¹⁸ and $[\text{Cu}(\text{bpy})_2(\text{NO}_3)](\text{NO}_3)$,²⁰ both α_4 and α_5 have been found to be less than 90° , in the range $87\text{--}84^\circ$. The equatorial ligands of CuB are thus seen to have a larger tetrahedral distortion than any of the other examples from this family of complexes, and one may describe the structure as intermediate between square pyramidal and compressed tetrahedral. The next step in this structural pathway would be to have O1B completely removed, resulting in a compressed tetrahedral CuN_4 chromophore; such a geometry is realized in $[\text{Cu}(\text{bpy})_2](\text{PF}_6)_2$.²⁶

Ligands and counter-ions. Average C–C and C–N bond lengths within the pyridine rings are 1.38 and 1.34 Å, respectively, which agree with values previously observed.^{27,28} The individual pyridine rings are essentially planar, and the dihedral angles between the pyridine rings in the four bipyridyl ligands are 9(2), 5(2), 3(3) and 8(2)°, in agreement with the range 0–13° previously reported for approximately symmetrically coordinated bipyridyl ligands.^{17,29} If one of the Cu–N bonds is appreciably longer than the other, a dihedral angle of up to 31.3° has been reported.²⁷ Owing to steric effects the two bipyridyl ligands cannot be coplanar. This constraint may be accommodated in a wide variety of coordination geometries. The bpy/bpy dihedral angles are 60.5 and 41.9° in the two differently distorted coordination spheres of CuA and CuB.

The average nitrate N–O bond length in the present structure is 1.243, in good agreement with the value of 1.245 Å generally quoted for the free nitrate ion.³⁰ The bond lengths are equal within experimental errors, despite the unsymmetrical coordination of this group. There is, however, a deviation from three-fold symmetry, as the O1A–CuA–O2 angle is 117° , while O1B–Cu1B–O2 is 122° , a fact which corroborates the assumption of unsymmetrical bidentate bonding to CuA.³⁰ The nitrate group is known to coordinate to metals in various modes; it appears both as a mono- and bidentate ligand, and as a bridging group.^{1,31} In the present case it acts as a bridging ligand in the *anti-anti* configuration ($\text{N5–O1A–CuA} = 113.5^\circ$, $\text{N5–O1B–CuB} = 124.7^\circ$), binding monodentately to one metal and in an asymmetric bidentate fashion to the other metal atom.

None of the three PF_6^- counter-ions is coordinated, but two of them are situated in approximate *trans* positions to the O2–CuA and O1B–CuB bonds, respectively, with $\text{Cu}\cdots\text{F}$ distances of 3.92 and 3.16 Å. Although these distances are too long to suggest even semicoordination, it may be noticed that analogous features are found for the non-coordinated nitrate and perchlorate ions in $[\text{Cu}(\text{bpy})_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$ ²⁰ and $[(\text{Cu}(\text{bpy})_2(\text{OH}))](\text{ClO}_4)_3$.²⁸ All three PF_6^- ions occupy general crystallographic positions, the average P–F distances in the three ions being 1.56, 1.58 and 1.51 Å, with individual variations up to ± 0.03 Å within each ion; the angles F–PA–F and F–PC–F are

within $\pm 3^\circ$ from 90 and 180° , while the F–PB–F angles deviate by up to $\pm 6^\circ$ from the values for a regular octahedron.

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