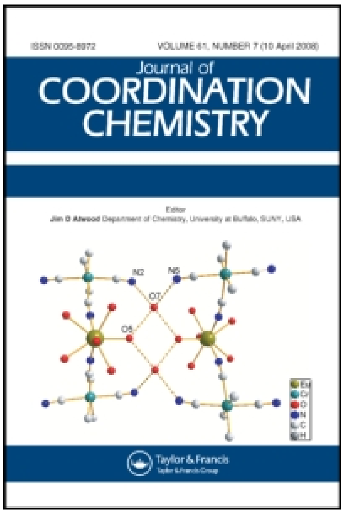

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Coordination geometry in bis(di-2-pyridylamine)copper(II) complexes. Crystal structures and spectroscopic properties of $[Cu(L)_2(NCS)_2][Cu(L)_2(NCS)]X$, X=, I^-

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Coordination geometry in bis(di-2-pyridylamine)copper(II) complexes. Crystal structures and spectroscopic properties of $[Cu(L)_2(NCS)_2][Cu(L)_2(NCS)]X$, $X = BF_4^-$, I^-

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The crystal structures of $[Cu(dpyam)_2(NCS)_2][Cu(dpyam)_2(NCS)](BF_4)$ (**1**) and $[Cu(dpyam)_2(NCS)_{1.14}I_{0.86}][Cu(dpyam)_2(NCS)_{0.77}I_{0.23}]I$ (**2**) (dpyam = di-2-pyridylamine) have been determined by single-crystal X-ray methods. Species **1** and **2** consist of two crystallographically independent Cu-bearing complexes, one being centrosymmetric and octahedrally elongated, and the other close to square pyramidal. The structures of both complexes and their EPR and electronic reflectance spectra are discussed and compared with those of related complexes.

Keywords: Copper(II); Di-2-pyridylamine; Thiocyanate; Crystal structure; Spectroscopic properties

1. Introduction

Cu(II) complexes are known to display a large variety of non-regular stereochemistries [1]. The complexes $Cu(chelate)_2X_2$ or $Cu(chelate)_2XY$ (chelate = 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen); X, Y = various anions, coordinated or not) exemplify this [1, 2] and much structural data are available [3–8]; structural data are more limited for corresponding complexes containing the more flexible ligand di-2-pyridylamine (dpyam) [5, 9–17]. The coordination geometry in the five-coordinate

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complexes [Cu(chelate)$_2$X]Y (chelate = bpy or phen) tends to be nearly regular trigonal bipyramidal with slight distortion towards square pyramidal ($\tau > 0.5$), e.g., [Cu(bpy)$_2$(NCS)](NO$_3$) ($\tau = 0.89$) [18], [Cu(bpy)$_2$(NCS)](NCS) ($\tau = 0.65$) [19], [Cu(bpy)$_2$(NCS)](BF$_4$) ($\tau = 0.61$) [20], [Cu(bpy)$_2$(NH$_3$)](BF$_4$)$_2$ ($\tau = 0.77$) [21] and [Cu(phen)$_2$(NCS)](ClO$_4$) ($\tau = 0.81$) [7]. With chelate = dpyam, complexes tend towards square-based pyramidal geometry with slight distortion towards trigonal bipyramidal ($\tau < 0.5$), e.g., [Cu(dpyam)$_2$(NCS)]$^+$ ($\tau = 0.18$) [15], [Cu(dpyam)$_2$-Cl]Cl · 4H$_2$O ($\tau = 0.25$) [12], [Cu(dpyam)$_2$(NCO)]$_2$(SO$_4$)(dpyam)$_2$ · H$_2$O ($\tau = 0.30$) [10], [Cu(dpyam)$_2$(NCS)](SCN) · 0.5DMSO ($\tau = 0.13$) [8] and [Cu(dpyam)$_2$Cl]$_2$I$_2$ · 2CH$_3$CN ($\tau = 0.32$) [11]. These observations demonstrate a noticeable difference between the chelate functions of bpy or phen and the more flexible dpyam ligand. In order to explore this relationship further, we report here the synthesis, crystal structures and electronic properties of the bis(dpyam) complexes [Cu(dpyam)$_2$(NCS)$_2$] [Cu(dpyam)$_2$(NCS)](BF$_4$) (**1**) and [Cu(dpyam)$_2$(NCS)$_{1.14}$I$_{0.86}$][Cu(dpyam)$_2$(NCS)$_{0.77}$- I$_{0.23}$]I (**2**).

2. Experimental

All reagents were commercial grade materials and used without further purification. Elemental analyses (C, H, and N) were determined on a Perkin-Elmer PE2400 instrument. IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer in the 4000–450 cm^{-1} region. Solid-state (diffuse reflectance) electronic spectra (polycrystalline samples) were recorded on a Perkin-Elmer Lambda2S spectrophotometer (8,000–18,000 cm^{-1}). X-band EPR spectra (polycrystalline samples) were recorded at room and liquid nitrogen temperatures with a Jeol RE2X spectrometer (X-band) by the Leiden University Study Werkgroep Fundamenteel Materialen Onderzoek.

2.1. *Synthesis*

Compounds **1** and **2** were prepared by essentially the same procedure. A dimethylformamide solution (10 cm^3) of Cu(I)SCN (0.065 g, 0.5 mmol) was added to a solution of di-2-pyridylamine (0.17 g, 1.0 mmol) in methanol (15 cm^3), followed by the addition of NaBF$_4$ (0.219 g, 2.0 mmol) or KI (0.332 g, 2.0 mmol), for **1** and **2**, respectively. The resulting green solution was allowed to evaporate at room temperature for two weeks, producing dark green needle crystals of [Cu(dpyam)$_2$(NCS)$_2$][Cu(dpyam)$_2$(NCS)](BF$_4$) (**1**) and [Cu(dpyam)$_2$(NCS)$_{1.14}$I$_{0.86}$] [Cu(dpyam)$_2$(NCS)$_{0.77}$I$_{0.23}$]I (**2**). The crystals were filtered off and dried in air. Anal. Calcd for **1** (%): C, 47.34; H, 3.35; N, 18.97. Found: C, 47.29; H, 3.34; N, 18.77. Calcd for **2** (%): C, 42.37; H, 3.05; N, 16.13. Found: C, 42.29; H, 2.97; N, 16.09.

2.2. *Crystallography*

Intensity data for **1** and **2** were collected at 293 K on a 4K Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at a detector distance of 6.0 cm and swing angle of −28°. A hemisphere of reciprocal space was covered by a combination of three sets of exposures; each set had a different ϕ angle (0, 88, 180°) and each exposure of 10 s for **1** and **2** covered 0.3° in ω. Data reduction and cell refinements were performed using SAINT [22]. An empirical absorption correction SADABS [23] was applied, which resulted in transmission coefficients ranging from 0.842 to 1.000 for **1** and from 0.689 to 1.000 for **2**. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 [24] software package.

For complex **2**, the NCS^- ligand coordinating Cu(1) has an occupancy factor of 0.77. Simultaneously there is an I^- ion practically coincident with the carbon atom of NCS^- with occupancy factor 0.23. The situation around Cu(2) is similar; NCS^- coordinating Cu(2) has an occupancy factor of 0.57 and I an occupancy factor of 0.43. The carbons of NCS groups were refined isotropically and the temperature factor of one of these fixed. Introducing the fractional I^- ion into the model caused the *R* value to drop from 0.120 to 0.075. All hydrogen atoms in **1** were located in a difference synthesis and refined isotropically, while all hydrogen atoms in **2** were fixed and allowed to ride on attached atoms. All non-H atoms were refined anisotropically except for the carbon atoms of thiocyanate groups in **2**. The BF_4^- anion in **1** is disordered, with two conformers having occupancy factors of 0.54 and 0.46. Crystal data and refinement details for **1** and **2** are listed in table 1. Selected bond lengths and angles are given in table 2. Figures 1 and 2 illustrate the structures of complexes **1** and **2**, respectively, and the atom numbering schemes used.

Table 1. Crystal data and refinement details for complexes **1** and **2**.

	1	**2**
Molecular formula	$C_{64}H_{54}B_2Cu_3F_8N_{22}S_4$	$C_{62.68}H_{54}Cu_3I_{3.32}N_{20.68}S_{2.68}$
Molecular weight	1623.84	1794.85
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.6529(6)	12.609(8)
b (Å)	14.3639(7)	14.020(8)
c (Å)	19.3375(10)	19.405(12)
β (°)	93.6170(10)	94.5940(10)
V (Å^3)	3507.5(3)	3419.4(4)
Z	2	2
D_{Calcd} (Mg m^{-3})	1.538	1.743
µ (mm^{-1})	1.100	2.561
$F(000)$	1650	1761
Crystal size (mm^3)	0.370 × 0.345 × 0.229	0.120 × 0.119 × 0.087
θ range (°)	1.61–28.31	1.62–28.27
Number of reflections collected	30,398	29,709
Number of unique reflections	8375 ($R_{\mathrm{int}} = 0.0253$)	8196 ($R_{\mathrm{int}} = 0.0574$)
Data/restraints/parameters	8375/0/601	8196/1/437
GOF	1.028	1.088
Final $R^{[a]}$ indices [$I > 2\sigma(I)$], wR_2	0.0521, 0.0752	0.0749, 0.1356
R indices (all data)^a	0.0664	0.1277
Largest diff. peak and hole (e Å^{-3})	0.894 and –0.941	1.261 and –0.660

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w\{|F_o - |F_c|\}^2 / w|F_o|^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

	1	**2**
Cu(1)–N(1)	1.992(3)	2.018(5)
Cu(1)–N(3)	2.010(2)	2.002(5)
Cu(1)–N(4)	2.140(3)	2.121(5)
Cu(1)–N(6)	2.016(3)	2.005(5)
Cu(1)–N(7)	1.989(3)	1.907(7)
Cu(2)–N(8)	2.024(2)	2.023(5)
Cu(2)–N(10)	2.019(2)	2.010(4)
Cu(2)–N(11)	2.417(3)	2.326(9)
N(1)–Cu(1)–N(3)	87.9(1)	89.3(3)
N(1)–Cu(1)–N(4)	103.7(1)	100.9(2)
N(1)–Cu(1)–N(7)	87.9(1)	156.4(3)
N(1)–Cu(1)–N(6)	167.9(2)	92.5(2)
N(3)–Cu(1)–N(4)	100.7(1)	102.2(2)
N(3)–Cu(1)–N(7)	156.9(1)	156.9(1)
N(3)–Cu(1)–N(6)	93.1(2)	169.6(2)
N(4)–Cu(1)–N(6)	88.0(2)	87.9(2)
N(4)–Cu(1)–N(7)	102.3(1)	102.6(3)
N(8)–Cu(2)–N(10)	94.7(2)	94.3(4)
N(8A)–Cu(2)–N(10)	85.4(2)	85.6(6)
N(11)–Cu(2)–N(8)	90.2(2)	86.9(3)
N(11)–Cu(2)–N(10)	87.1(1)	88.2(3)
N(11)–Cu(2)–N(8A)	89.8(1)	93.1(3)
N(11)–Cu(2)–N(10A)	92.9(1)	91.8(3)
N(11)–Cu(2)–N(11A)	180.0(3)	180.0(1)
N(11A)–Cu(2)–N(8)	89.8(2)	93.1(3)
N(11A)–Cu(2)–N(10)	92.9(1)	91.8(3)
N(11A)–Cu(2)–N(8A)	90.2(2)	86.9(3)
N(11A)–Cu(2)–N(10A)	87.1(1)	88.2(3)

3. Results and discussion

3.1. *Crystal structures*

Complexes **1** and **2** contain the two crystallographically independent units [$Cu_{0.5}$(dpyam)(NCS)] and [$Cu_{0.5}$(dpyam)$(NCS)_{0.57}I_{0.43}$] (the other halves being inversion related), $[Cu(dpyam)_2(NCS)]^+$ and $[Cu(dpyam)_2(NCS)_{0.77}I_{0.23}]^+$ cations and non-coordinated BF_4^- and I^- anions for **1** and **2**, respectively. The two crystallographically independent Cu(II) ions possess totally different coordination geometries.

Molecules A consist of $[Cu(dpyam)_2(NCS)]^+$ cations and BF_4^- anions for complex **1** (figure 1a); and $[Cu(dpyam)_2(NCS)_{0.77}I_{0.23}]^+$ cations and I^- anions for complex **2** (figure 2a). Cu(1) atoms of $[Cu(dpyam)_2(NCS)]^+$ in **1** and $[Cu(dpyam)_2(NCS)_{0.77}I_{0.23}]$ cation in **2** are five-coordinate, with approximately square pyramidal stereochemistry. The four in-plane bond lengths are not significantly different; Cu–N distances vary from 1.989(3) to 2.016(2) Å for **1** and 1.909(7) to 2.019(5) Å for **2**. The fifth ligand bond length, Cu(1)–N(4), is significantly different, with a value of 2.140(1) Å for **1** and 2.120(5) Å for **2**. The distance Cu(1)–I(1) for **2**, in which I^- is practically coincident with the C atom of NCS^- ligand with occupancy factor 0.23, is 2.996(1) Å. The τ value defined to describe the degree of trigonal distortion is 0.18 for **1** and 0.22 for **2** ($\tau = (\beta - \alpha)/60$ where β and α are the largest coordination angles [6]). As the regular

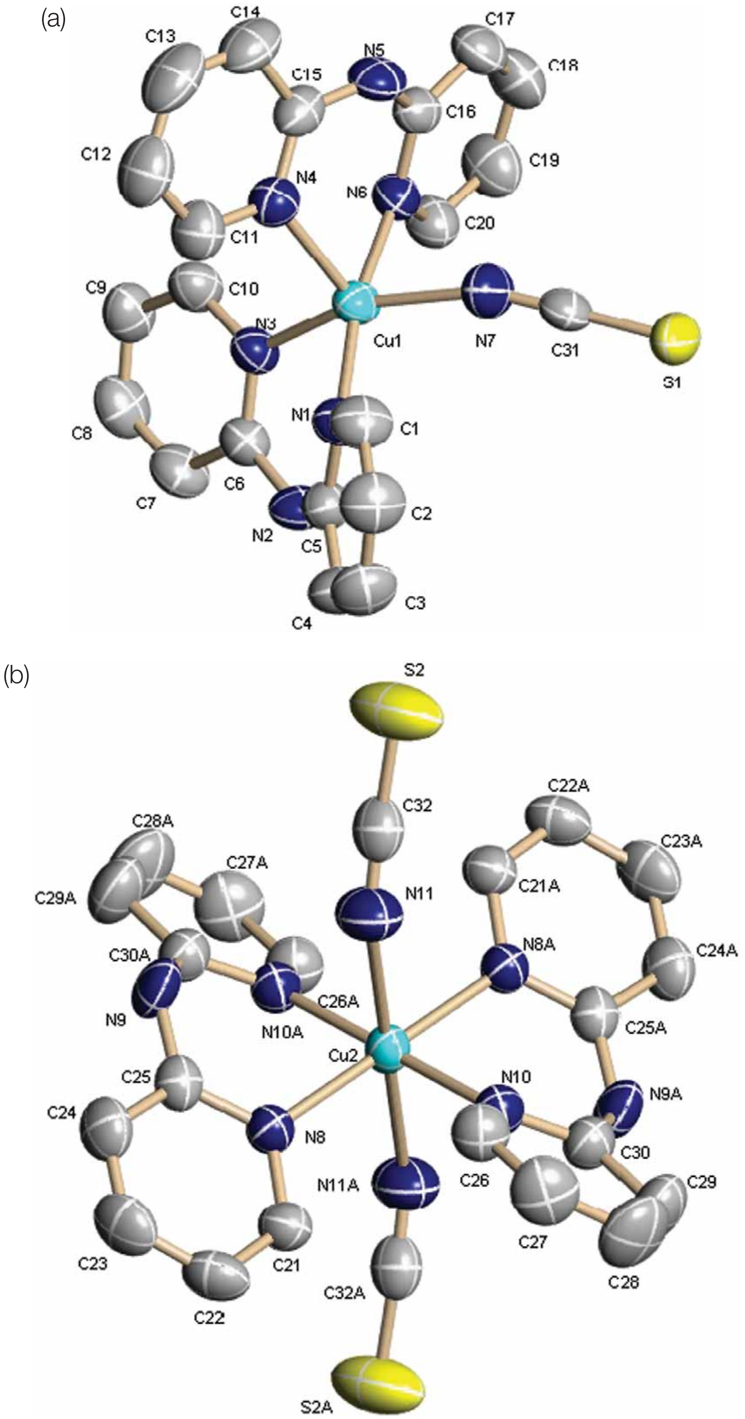

Figure 1. ORTEP plots (50% probability level) of the copper species in $[Cu(dpyam)_2(NCS)_2][Cu(dpyam)_2(NCS)]BF_4$ (**1**). (a) The chromophore of [Cu(dpyam)2(NCS)]+ in 1; (b) The chromophore of [Cu(dpyam)2 (NCS)2 in 1. Hydrogen atoms and the uncoordinated BF_4^- ion are omitted for clarity.

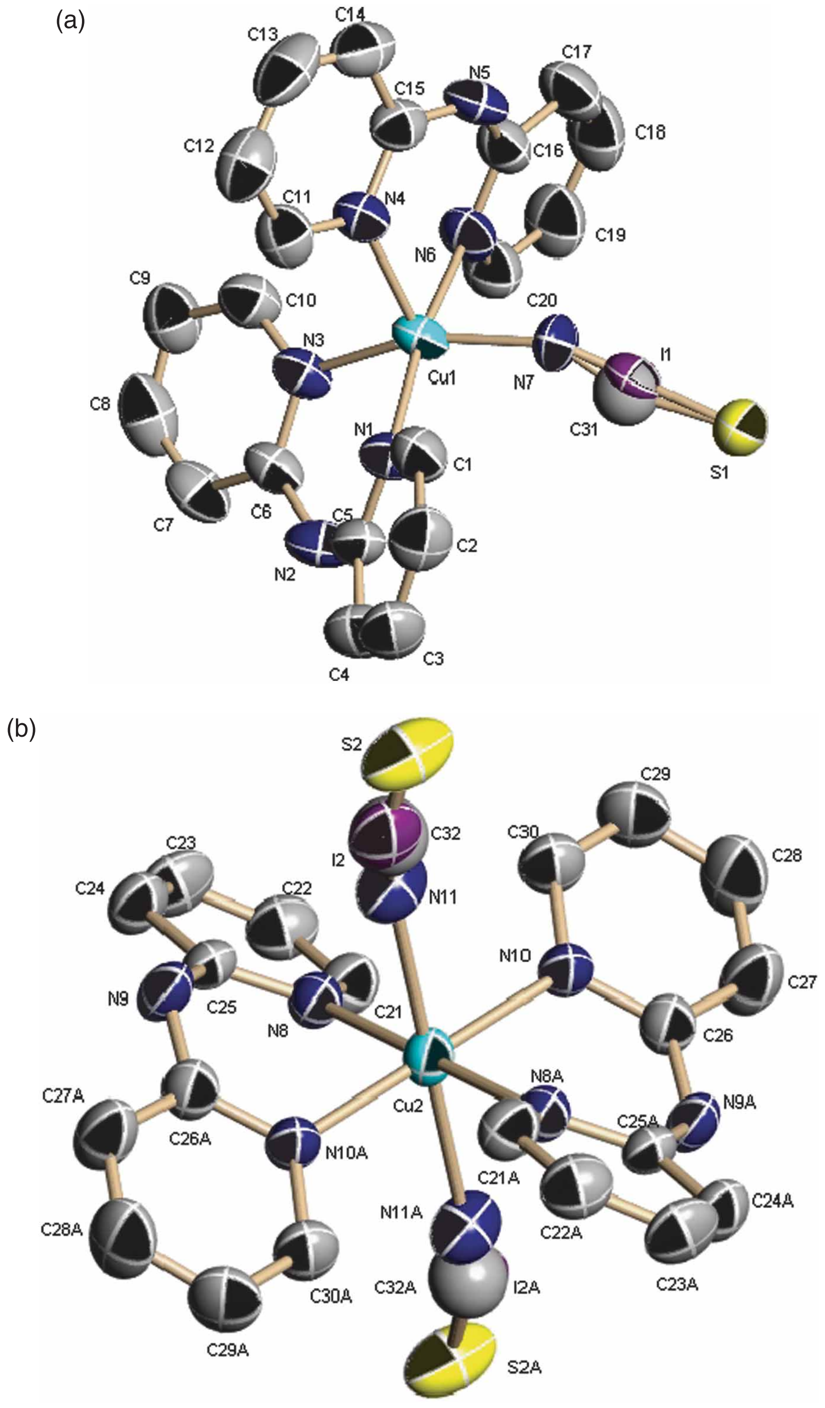

Figure 2. ORTEP plots (50% probability level) of the copper species in [Cu(dpyam)$_2$(NCS)$_{1.14}$(I)$_{0.86}$][Cu(dpyam)$_2$(NCS)$_{0.77}$I$_{0.23}$]I (**2**). (a) The chromophore of [Cu(dpyam)2(NCS)] + in 2; (b) The chromophore of [Cu(dpyam)2 (NCS)2 in 2. Hydrogen atoms and uncoordinated iodide ions are omitted for clarity.

Table 3. Hydrogen bonding details (Å, °) for **1** and **2**.

D–H···A	D–H	H···A	D···A	∠DHA	A	
1						
N9–H25	0.71(2)	2.19(1)	2.88(2)	167(2)	F1	$[x, -y+1/2, z+1/2]$
N9–H25	0.71(2)	2.49(2)	3.18(2)	167(2)	F1A	$[x, -y+1/2, z+1/2]$
N5–H15	0.64(2)	2.80(1)	3.43(1)	171(1)	S2	
N2–H5	0.69(2)	2.78(1)	3.46(1)	172(2)	S1	$[-x, -y+1, -z]$
2						
N5–H15	0.860	2.667	3.41(1)	145.31	S2	$[x, -y+3/2, z-1/2]$
N2–H5	0.860	2.815	3.47(1)	134.99	S1	$[-x+1, -y+1, -z+1]$

trigonal bipyramid and square pyramid have τ values of 1.00 and 0.00, respectively, the stereochemistry of the CuN_4N' chromophore of both compounds is best described as square pyramidal with slight trigonal distortion. The Cu(II) ions of **1** and **2** are displaced 0.30(1) and 0.29(1) Å from the basal planes toward the fifth ligand positions. Dihedral angles between the pyridine rings in the same dpyam ligand are 32.9(1) and 22.4(1)° for **1** and 32.8(1) and 22.1(2)° for **2**, the large differences serving to accommodate the square pyramidal arrangement. The N–Cu–N bite angles of the dpyam ligands are 87.9(1) and 88.0(2)° for **1** and 87.9(1) and 87.9(5)° for **2**.

In molecules B, each copper atom in **1** and **2** is six-coordinate, $[Cu(dpyam)_2(NCS)_2]$ (figure 1b) and $[Cu(dpyam)_2(NCS)_{1.14}I_{0.86}]$ (figure 2b), respectively. The copper(II) ion is equatorially bonded to two didentate dpyam ligands, situated at a centre of symmetry [Cu(2)–N(8) and Cu(2)–N(10) = 2.024(1) and 2.019(1) Å for **1** and 2.023(1) and 2.010(1) Å for **2**] and axially bonded to the isothiocyanato group [Cu(2)–N(11) = 2.417(3) Å for **1**], while the axial positions of **2** are occupied by nitrogen atoms of SCN^- groups with a population parameter of 0.57. The Cu(2)–N(11) distance is 2.326(3) Å, giving a tetragonally elongated stereochemistry with tetragonality (T = mean in-plane Cu–N distance/mean out-of-plane Cu–N distance) of 0.84 and 0.87 for **1** and **2**, respectively. As discussed above, iodide groups with an occupancy of 0.43 were fitted to remaining electron density at the axial sites. Uncoordinated iodide ions have a Cu(2)–I(2) distance of 3.651(1) Å. Each basal CuN_4 plane of both compounds is exactly planar, attributed to the large dihedral angle (38.3(2)° for **1** and 37.9(4)° for **2**), between the pyridine rings of the dpyam ligand. This large dihedral angle indicates that the more flexible dpyam ligand allows is responsible for the adoption of the particular geometry. N–Cu–N bite angles of the dpyam ligands are 94.7(2) and 94.3(4)° for **1** and **2**, respectively.

The τ values (0.18 and 0.22) for the slightly trigonal bipyramidal-distorted square-based pyramidal (TBDSBP) CuN_4N' chromophores of **1** and **2** (figures 1a and 2a) are comparable (table 4) to those found in the related complexes $[Cu(dpyam)_2Cl]Cl \cdot 4H_2O$, $[Cu(dpyam)_2(NCO)]_2(SO_4)(dpyam)_2 \cdot H_2O$, $[Cu(dpyam)_2(NCS)](SCN) \cdot 0.5DMSO$ and $[Cu(dpyam)_2Cl]_2I_2{\cdot}2CH_3CN$, as noted above. The geometry of the latter compound should be TBDSBP rather than distorted trigonal bipyramidal as previously reported [11]. In the corresponding compounds $[Cu(dpyam)_2Cl]Cl$ ($\tau = 0.57$) [14] and $[Cu(dpyam)_2I]_2I(ClO_4)$ ($\tau = 0.63$ and 0.65) [13], the intermediate geometry slightly distorted toward the trigonal bipyramid is considerably more pronounced, giving the square-based pyramidal-distorted trigonal bipyramidal (SBPDTB) stereochemistry.

There is a substantial number of monomeric five-coordinate $[Cu(bpy/phen)_2X]^+$ complexes with coordination geometries ranging from TBDSBP ($\tau = 0.19$–0.22)

Table 4. Structural and spectroscopic data for selected five-coordinate copper(II) complexes.

					Polycrystalline ESR spectrum			
Complex	Chromophore	Geometry	τ	Band maxima (kK)[c]	g_1	g_2	g_3	Reference
$[Cu(dpyam)_2(NCS)](BF_4)$ (**1**)[a]	CuN_4N'	TBDSBP	0.18	15.66, 10.71		2.107[d]		This work
$[Cu(dpyam)_2(NCS)_{0.77}I_{0.23}]$ (**2**)	CuN_4N'	TBDSBP	0.22	14.53, 10.33		2.107[d]		This work
$[Cu(dpyam)_2(NCS)](SCN) \cdot 0.5DMSO$	CuN_4N'	TBDSBP	0.13	15.74, 10.66	2.310		2.054	[8]
$[Cu(dpyam)_2(NCO)]_2(SO_4)(dpyam)_2 \cdot H_2O$	CuN_4N'	TBDSBP	0.30	14.23, 10.63		2.083		[10]
$[Cu(dpyam)_2(NCS)_{1.5}(ClO_4)_{0.5}]$	CuN_4N'	TBDSBP	0.18					[15]
$[Cu(dpyam)_2Cl]Cl \cdot 4H_2O$	CuN_4Cl	TBDSBP	0.25					[12]
$[Cu(dpyam)_2Cl]_2I_2 \cdot 2CH_3CN$	CuN_4Cl	TBDSBP	0.32					[11]
$[Cu(dpyam)_2Cl]Cl$	CuN_4Cl	Intermediate	0.57					[14]
$[Cu(dpyam)_2I]_2I(ClO_4)$[b]	CuN_4I	SBPDTB	0.63, 0.65					[13]
$[Cu(phen)_2Cl](BPh_4)$	CuN_4Cl	TBDSBP	0.19	14.50, 11.50				[6b]
$[Cu(phen)_2Br](BPh_4)$	CuN_4Br	TBDSBP	0.22	14.40, 10.70				[6d]
$[Cu(phen)_2(NCS)](ClO_4)$	CuN_4N'	Near RTB	0.97					[7]
$[Cu(phen)_2Br]Br \cdot H_2O$	CuN_4Br	Near RTB	0.87					[29]
$[Cu(bpy)_2(NCS)](NO_3)$	CuN_4N'	Near RTB	0.89					[18]
$[Cu(bpy)_2(NCS)](NCS)$	CuN_4N'	SBPDTB	0.65					[19]
$[Cu(bpy)_2(NCS)](BF_4)$	CuN_4N'	SBPDTB	0.61					[20]
$[Cu(bpy)_2(NH_3)](BF_4)_2$	CuN_4N'	SBPDTB	0.67		0			[21]

[a] TBDSBP to TBDSBP (TBDSBP = trigonal bipyranidal distorted square base pyramidal); [b] SBPDTP to SBPDTB (SBPDTB = square based pyramidal distored trigonal bypyramidal; [c] (cKK) to (KK) (cKK = 1000 cm^{-1}, dgi (determination from pseudo-isotropic sepctra)).

to SBPDTB ($\tau = 0.56$–0.80), and to near regular trigonal bipyramidal (RTB) ($\tau = 0.80$–1.00) [6]. However, most of them have geometries ranging from SBPDTB to near RTB. There are only two complexes having geometry very close to TBDSBP, [Cu(phen)$_2$Cl](BPh$_4$) ($\tau = 0.19$) [6b] and [Cu(phen)$_2$Br](BPh$_4$) ($\tau = 0.22$) [6d]. Related CuN$_4$N′ chromophores in [Cu(bpy)$_2$(NCS)](NO$_3$) · H$_2$O, [Cu(bpy)$_2$(NCS)](NCS), [Cu(bpy)$_2$(NCS)](BF$_4$), [Cu(bpy)$_2$(NH$_3$)](BF$_4$)$_2$ and [Cu(phen)$_2$(NCS)](ClO$_4$) also involve the above range, as noted above. It thus appears that near RSBP and TBDSBP geometries are better attained with the more flexible di-2-pyridylamine ligand.

The elongated centrosymmetric octahedral geometry found in **1** and **2** ($T = 0.83$ and 0.87) has also been observed in [Cu(dpyam)$_2$X$_2$] (X = tricyanoethyleneoate) [25] (table 5), [Cu(dpyam)$_2$(NCS)$_2$] ($T = 0.83$) [15], [Cu(dpyam)$_2$(N$_3$)$_2$] ($T = 0.81$) [26], [Cu(dpyam)$_2$(NO$_3$)$_2$] ($T = 0.81$) [15], [Cu(dpyam)$_2$(Br)$_2$] · 2H$_2$O ($T = 0.65$) [11], [Cu(dpyam)$_2$(SCN)$_2$] ($T = 0.69$) [8], [Cu(dpyam)$_2$(OH$_2$)$_2$](SO$_4$) · 7H$_2$O ($T = 0.81$, 0.82) [27] and [Cu(dpyam)$_2$(OH$_2$)$_2$](PF$_6$)$_2$ ($T = 0.82$) [9a]. The complexes [Cu(dpyam)$_2$(CF$_3$SO$_3$)$_2$] ($T = 0.81$) [9a] and [Cu(dpyam)$_2$(OH$_2$)$_2$](S$_4$O$_6$) ($T = 0.82$) [9a], which are not centrosymmetric, have similar structures. The planar equatorial CuN$_4$ planes of these complexes are only possible because of the flexibility of the dpyam ligands. This results in a greater range of values of dihedral angles between the pyridine rings, which are nonetheless comparable for all complexes (35.6–46.5°).

Analogous coordination geometry has not been found in complexes of bpy and phen. [Cu(bpy)$_2$(ClO$_4$)](ClO$_4$) [27] and [Cu(bpy)$_2$(BF$_4$)](BF$_4$) [27], although involving a six-coordinate, elongated octahedral chain structure, are not centrosymmetric and show strong tetrahedral distortion of the square base (dihedral angles = 37.9 and 44.6°, respectively). Coordination geometries in [Cu(bpy)$_2$(NO$_3$)](NO$_3$) · H$_2$O [28] and [Cu(phen)$_2$Br]Br · H$_2$O [29] are totally different from those of the closely related dpyam complexes [Cu(dpyam)$_2$(NO$_3$)$_2$] [15] and [Cu(dpyam)$_2$Br$_2$] · 2H$_2$O [11]. The former involves a distorted bicapped square pyramidal geometry of the CuN$_4$OO′ chromophore with marked asymmetric bidentate coordination of the nitrato group, while the latter involves a five-coordinate CuN$_4$Br complex of near RTB geometry with slight distortion towards square pyramidal ($\tau = 0.87$). These observations again demonstrate a noticeable difference between the chelate functions of bpy or phen and the more flexible dpyam ligand.

In the present cases, in both six- and five-coordinate units, the isothiocyanate groups coordinate in a bent end-on fashion, Cu–N–C angles being 159.8(1)° for **1** and 144.8(2)° for **2** for molecule A, and 159.8(1)° for **1** and 151.8(6)° for **2** for molecule B. The crystallographically independent amine groups are all involved in weak hydrogen bonding (table 3).

3.2. *Spectroscopy*

X-band EPR spectra measured on polycrystalline samples at RT and 77 K showed in both compounds a broad isotropic signal with a g_{iso} at around 2.10, giving no information regarding the electronic ground state. Polycrystalline electronic reflectance spectra of **1** and **2** show a high-energy peak at 15,660 and 14,530 cm^{-1}, with a low energy peak of low intensity at 10,710 and 10,330 cm^{-1}, respectively, consistent with the mixed geometries [6]. The absorption maximum of **1** is at higher energy than that of **2**

Table 5. Structural and spectroscopic data for selected tetragonally distorted octahedral copper(II) complexes.

Complex	Chromophore	Tetragonality (T)	Band maxima (kK^a)	Polycrystalline ESR spectrum			References
				g_1	g_2	g_3	
$[Cu(dpyam)_2(NCS)_2]$ (**1**)	CuN_4N_2	0.83	15.66, 10.71		2.107		This work
$[Cu(dpyam)_2(NCS)_{1.14}(I)_{0.86}]$ [(**2**)	CuN_4N_2	0.87	14.53, 10.33		2.107		This work
$[Cu(dpyam)_2X_2]$	CuN_4O_2	0.83					[25]
$[Cu(dpyam)_2(NCS)_2]$	CuN_4N_2	0.83					[15]
$[Cu(dpyam)_2(N_3)_2]$	CuN_4N_2	0.81	17.30	2.25		2.06	[26]
$[Cu(dpyam)_2(NO_3)_2]$	CuN_4O_2	0.81					[15]
$[Cu(dpyam)_2(Br)_2] \cdot 2H_2O$	CuN_4Br_2	0.65					[11]
$[Cu(dpyam)_2(SCN)_2]$	CuN_4S_2	0.69	16.70, 14.08				[8]
$[Cu(dpyam)_2(OH_2)_2](SO_4) \cdot 7H_2O$	CuN_4O_2	0.81, 0.82					[27]
$[Cu(dpyam)_2(OH_2)_2](PF_6)_2$	CuN_4O_2	0.82	14.97, 10.13	2.47		2.08	[9a]
$[Cu(dpyam)_2(CF_3SO_3)_2]$	CuN_4O_2	0.81	18.12, 15.43	2.18		2.06	[9a]
$[Cu(dpyam)_2(OH_2)_2](S_4O_6)$	CuN_4O_2	0.82	17.98, 14.79	2.26		2.09	[9a]
$[Cu(bpy)_2(O_2ClO_2)](ClO_4)$	CuN_4O_2	0.757	15.10	2.054^b	2.065^b	2.255^b	[27]
$[Cu(bpy)_2(F_2BF_2)](BF_4)$	CuN_4F_2	0.763	15.20	2.055^b	2.070^b	2.243^b	[27]

[a] (aKK) to (KK) (aKK) = 1000 cm^{-1}); [b] 2.054b, 2.065b, 2.255b…,2.055b, 2.070b, 2.243b (single crytal e.s.r. values, cgi).

due to greater distortion toward RSBP of the five-coordinate unit and the more pronounced tetragonal elongation of the six-coordinate unit. However, the structure and electronic spectrum of **1** are similar to those of the closely related compound $[Cu(dpyam)_2(NCS)](SCN) \cdot 0.5DMSO$ (15,740 and 10,660 cm^{-1}) ($\tau = 0.13$) [8] and those of **2** are comparable to those of the closely related compound $[Cu(dpyam)_2(NCO)]_2(SO_4(dpyam) \cdot H_2O$ (14,230 and 10,630 cm^{-1}) ($\tau = 0.30$) [10]. IR spectra show a strong split band ($\nu_{as}(CN)$) at 2090 and 2072 cm^{-1} for **1**, and 2090 and 2073 cm^{-1} for **2**. Several weak $\nu_s(CS)$ bands at 845, 776 and 744 cm^{-1} for **1**, and 869, 774 and 744 cm^{-1} for **2** are observed. The IR spectrum of **1** also shows a strong band at approximately 1094 cm^{-1} due to the tetrafluoroborate ion.

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 285348 and 285349 for **1** and **2**, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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