Crystal structures, spectro-structural correlation and structural pathways of eight \([\text{Cu(dpyam)}_2(\text{NCO})][Y]\) complexes (dpyam = di-2-pyridylamine), \(Y = \text{Br}^–, \text{CF}_3\text{SO}_3^–, \text{BF}_4^– \cdot \text{dpyam}, \text{Cl}^– \cdot 4\text{H}_2\text{O}, \text{NO}_3^–, \text{PF}_6^–, \text{ClO}_4^– \text{and BPh}_4^–\)

Sujittra Youngme \(^{a,*}\), Jaturong Phatchimkun \(^a\), Unchulee Suksangpanya \(^a\), Chaveng Pakawatchai \(^b\), Narongsak Chaichit \(^c\), Palangpon Kongsaeere \(^d\), Jurek Krzystek \(^e\), Brian Murphy \(^f\)

\(^a\) Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
\(^b\) Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand
\(^c\) Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand
\(^d\) Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand
\(^e\) National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, United States
\(^f\) Department of Chemistry, College of Science, United Arab Emirates University, P.O. Box 17551, Al-Ain, United Arab Emirates

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Abstract

The crystal structures of eight new \([\text{Cu(dpyam)}_2(\text{NCO})][Y]\) complexes which \(Y = \text{Br}^– (1), \text{CF}_3\text{SO}_3^– (2), \text{BF}_4^– \cdot \text{dpyam} (3), \text{Cl}^– \cdot 4\text{H}_2\text{O} (4), \text{NO}_3^– (5), \text{PF}_6^– (6), \text{ClO}_4^– (7) \text{and BPh}_4^– (8), \) respectively have been determined by X-ray crystallography. Five of the complexes, 1–5 (\(\tau = 0.09–0.30\)) have a CuN\(_4\)N\(_0\) chromophore with a trigonal bipyramidal distorted square based pyramidal (TBDSBP) stereochemistry, 6 and 7 (\(\tau = 0.53–0.54\)) involve an intermediate five-coordinate stereochemistry, while 8 (\(\tau = 0.76\)) involves a square base pyramidal distorted trigonal bipyramidal (SBPDTB) stereochemistry. The structures of 1–8 are compared by scatter-plot analysis with \([\text{Cu(dpyam)}(\text{NCO})][\text{SO}_4]^{0.5} \cdot \text{dpyam}^{0.5} \cdot 4\text{H}_2\text{O} (9), the only complex of known crystal structure within this series reported to date. Scatter plots of the cations distortion isomers of the \([\text{Cu(dpyam)}_2(\text{NCO})][Y]\) series of complexes suggests that all nine complexes lie on a common structural pathway, involving a mixture of symmetric, \(v_{\text{sym}}\), \(C_2\) mode and asymmetric, \(v_{\text{asym}}\), non-\(C_2\) modes of vibration of the CuN\(_4\)N\(_0\) chromophore. The resulting linear and parallel structural pathways are consistent with the direct observation of the effect of vibronic coupling on the stereochiristries of the complexes, which can range from SBPDTB to TBDSBP which correlate with electronic spectral data. The EPR spectra (K-band and V-band) of complexes 1–7 are in rhombic type, while complex 8 is axial with \(g_L = 2.185\) and \(g_J = 2.005\), consistent with a \(d_{z^2}\) ground state for the approximately trigonal bipyramidal stereochemistry of the CuN\(_4\)N\(_0\) chromophore. These are in agreement with electronic reflectance spectra of the complexes and correspond to their stereochiristries.

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1. Introduction

One of the consequences of the Jahn-Teller theorem [1] in the stereochemistry of the copper(II) ion has been termed the plasticity effect [2] which suggests that the various distortion isomers of the copper(II) ion are related
by soft modes of vibration of the more regular stereochemistries. Hence, the concept of a structural pathway [3–5]. Fig. 1, for [Cu(chelate)₂X][Y] type complexes has been developed. In 1984, Addison, Reedijk and co-workers introduced a very useful parameter, τ, which provides a measure of the degree of square-based pyramidal (SBP) versus trigonal bipyramidal (TBP) geometry adopted by five-coordinate Cu(II) complexes [6]. This parameter provides a convenient tool for comparing structures of similar five-coordinate Cu(II) complexes. The parameter τ is defined as (β − α)/60, where β and α are the largest coordination angles, and its value varies from 0 (in regular SBP) to 1 (in regular TBP). The molecular structures of five-coordinate copper(II) complexes range extensively from regular trigonal bipyramidal (RTBP, D₃h) to regular square based pyramidal (RSBP, C₄v) with most complexes falling between these two stereochemistries [7], somewhere along the classical Berry pathway [6,8]. This feature can be useful in probing the relationships between structural correlations and the respective structural pathway involving vibronic type coupling.

In the majority of [Cu(chelate)₂X][Y] complexes the differences in stereochemistry may be associated with the differences in the ligands present i.e. chelate = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and di-2-pyridylamine (dpyam) and X = Cl⁻, Br⁻, I⁻ or H₂O, respectively. A number of structural pathways of various copper(II) five-coordinate series, [Cu(bipy)₂X][Y] and [Cu(phen)₂X][Y] have now been reported in the literature [3,9]. These systems represent various types of structural pathways and such structural correlations have been found to be consistent with spectroscopic data involving EPR and electronic reflectance spectra. However, structural studies and structural correlations involving five-coordinate complexes containing the more flexible dpyam ligand and a pseudohalide, such as NCO⁻ have not been reported to date in the literature. Moreover, the square pyramidal geometry in new dpyam complexes is inherently different from previously reported five-coordinate square pyramidal geometries involving copper(II) and other chelate ligands [3,9]. The axial position of the square pyramid in this complex series is the occupied by dpyam nitrogen which is different from those of the bipy and phen series to which the halide or H₂O is occupied. Hence, it is of interest to look at potential structural correlations and investigate the existence of a potential structural pathway for the series of five-coordinate copper(II) complexes of the type, [Cu(dpyam)₂(NCO)]⁺[Y].

2. Experimental

2.1. General

The ligand, di-2-pyridylamine and all reagents are commercial grade materials and were used without further purification. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer as KBr disc in the 450–4000 cm⁻¹ spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda 2S spectrometer, over the range 8000–18000 cm⁻¹. X-band electron paramagnetic resonance (EPR) measurements were performed at room temperature on a JEOL RE2X spectrometer, using DPPH (g = 2.0036) as a standard. Higher EPR frequencies were employed in experiments conducted at 77 K: K-band (~27 GHz), V-band (~54 GHz) and W-band (~100 GHz). In this case a transmission single-pass home-made spectrometer based on a superconducting magnet was used [10]. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE2400 CHNS/O.
A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (15 cm³) of CuBr₂ (0.071 g, 0.5 mmol). Solid KNCO (0.162 g, 2.0 mmol) was then added to the reaction mixture. The solution was allowed to evaporate at room temperature. After several days, dark green rod-shaped crystals of 6 were formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 90%. Anal. Calc. for C₂₅H₂₆N₇CuO₅Cl: C, 49.41; H, 3.11; N, 16.68. Found: C, 49.58; H, 2.99; N, 16.68%.

Caution: perchlorates are explosive!

A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (10 cm³) of Cu(NO₃)₂ · nH₂O (0.091 g, 0.5 mmol). Solid KNCO (0.081 g, 1.0 mmol) was then added. The green solution was slowly evaporated at room temperature. After two weeks, green rod-shaped crystals of 8 formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 80%. Anal. Calc. for C₄₅H₃₈N₇CuOB: C, 70.45; H, 4.99; N, 12.78%.

2.2. Crystallography

The X-ray single-crystal data of complexes 1-3 and 5-8 were collected at 293 K on a 4 K Bruker SMART CCD area-detector diffractometer rotating anode, graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the SMART program [11]. Data reduction and cell refinements were performed using the program SAINT [12]. An empirical absorption correction was applied using the SADABS [13] program, which resulted in transmission coefficients ranging from 0.854 to 1.000 for 1, 0.402 to 1.000 for 2, 0.774 to 1.000 for 3, 0.811 to 1.000 for 5, 0.890 to 1.000 for 6, 0.834 to 1.000 for 7 and 0.898 to 1.000 for 8. The unit-cell parameters of complex 4 were determined and the intensity data collected on an Enraf-Nonius MACH3 diffractometer with Mo Kα radiation (λ = 0.7083 Å) at 298 K. An absorption correction was performed using the ψ-scan program, which resulted in transmission coefficients ranging from 0.904 to 1.000. All eight structures were solved by direct methods and refined by full-matrix least-squares method on \( F_{o}^{2} \) with...
anisotropic thermal parameters for all nonhydrogen atoms using the sHELXTL-PC V 6.12 [14] software package. All hydrogen atoms in 1–8 were located by difference synthesis and refined isotropically, except the hydrogen atoms of the water molecules in 4, which we were unable to locate and not fix. The molecular graphics were created using sHELXTL-PC. The O atom in isocyanato group of 2 and 3 showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5 and 0.5 for 2 and 0.7 and 0.3 for 3. The F and O atoms of the trifluoromethanesulfonate group of 2 showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5 and 0.5, respectively. The F atoms of the tetrafluoroborate group of 3 and hexafluorophosphate group of 6 also showed disorder. They were divided into two sets with occupancies of 0.5 and 0.5. The O atoms of the perchlorate group of 7 showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5 and 0.5, respectively. The crystal and refinement details for complexes 1–8 are given in Table 2 . Fig. 2 shows a representative molecular structure for the [Cu(dpyam)2(NCO)]⁺ cation, the atomic numbering scheme and the angle notation used.

3. Results and discussion

3.1. Crystal structures

The asymmetric unit of complexes 1–8 involves a [Cu(dpyam)₂(NCO)]⁺ cation and Br⁻, CF₃SO₃⁻, BF₄⁻, dpyam, Cl⁻·4H₂O, NO₃⁻, PF₆⁻, ClO₄⁻ and BPH₄⁻ anions, respectively in the lattice. In addition, 3 and 4 involve one dpyam molecule and four water molecules in the unit cell, respectively. None of the anions or water molecules is close enough (<3.0 Å) to be considered even weakly semi-coordinated to the copper(II) cation [15].

The structure of the cations all involve a five-coordinate Cu₅N₄ stereochemistry, with a square pyramidal stereochemistry having a trigonal bipyramidal distorted square based pyramidal stereochemistry (TBDSBP) in 1–5, an intermediate five-coordinate stereochemistry for 6 and 7, and a square based pyramidal distortion (SBPDTB) for 8. All eight complexes are further examples of distortion isomers of the [Cu(dpyam)₂(NCO)]⁺ cation, whose stereochemistries are related by the structural pathways of Fig. 1. No attempt will be made to describe the individual structures of complexes 1–8, Table 2 , but scatter-plot analysis will be used to compare their structures with that of [Cu(dpyam)₂(NCO)]SO₄·0.5·dpyam·0.5H₂O (9) the only other complex of known crystal structure [16]. Table 2 summarises the selected bond lengths and bond angles of all eight complexes, sequenced in order of their τ values, where

\[
\tau = (s_8 - x_1)/60 \quad [6],
\]

and Table S1 summarises the maximum, minimum, difference (Δ) and average bond length and bond angle values for the series of nine [Cu(dpyam)₂(NCO)]⁺[Y] complexes. Table S3 gives the sums of the in-plane bond angles, and bond distances, Cu–N(2), Cu–N(4) and Cu–N', respectively.

3.2. The [Cu(dpyam)₂(NCO)]⁺[Y] data

The structures of the nine five-coordinate Cu₅N₄ stereochemistries vary from TBP to near SBP, reflected in a range of τ values of 0.76–0.09, Δτ = 0.67. This is a substantial variation in τ, the largest seen to date for the cation distortion isomers of the [Cu(dpyam)₂X][Y] series of complexes [17]. None of the complexes has a near RTB (regular trigonal bipyramidal) stereochemistry or lies on a twofold axis of symmetry. Six complexes (1–5 and 9) have τ values in the more limited range of 0.09 to 0.31 and their stereochemistries are best described as TBDSBP. Complexes 6 and 7 have τ values of 0.53 and 0.54 and their stereochemistries are best described as intermediate five coordinate. Complex 8 has a τ value of 0.76 and its stereochemistry is best described as SBPDTB.

Relative to a RTB stereochemistry, the out-of-plane distances, Table 2 , show only small differences, Table S1 , with ΔCu–N(1) = 0.030 Å and ΔCu–N(3) = 0.044 Å. The largest variations in bond lengths are present in the equatorial bond distances Cu–N(4), Cu–N' and Cu–N(2), respectively. The Cu–N(4) distances show the least variation ranging from 2.089(1) to 2.283(3) Å, with Δ = 0.194 Å and with an average value = 2.182(3) Å. The Cu–N(2) distances vary from 2.014(10) to 2.074(2) Å, with Δ = 0.060 Å and with a mean value = 2.044(2) Å. The Cu–N' distances range from 1.903(3) to 1.984(1) Å, with Δ = 0.081 Å and with an average value = 1.947(1) Å. The average of the in-plane Cu–N(2,4,N') distances, 2.057(2) Å, is greater than the average of the axial Cu–N(1,3) distances, 2.015(1) Å, by 0.042 Å, consistent with a TB stereochemistry and slightly lesser than the difference of 0.1 Å normally observed [18]. The out-of-plane bond angles, Table 2 , show only small differences, Table S1 , with Δα = 0.7 and Δβ = 0.10 ranging from 3.6° to 6.5° and 6.2–15.4°, respectively. The x₁ in-plane angles show the largest variation ranging from 124.7(2)° to 167.1(1)°, with Δ = 42.4° and with a mean value = 151.8(1)°. The x₂ in-plane angles show the smallest variation ranging from 98.8(2)° to 119.4(1)°, with Δ = 20.6° and average = 108.4(1)°. The x₃ angles vary from 93.7(1)° to 115.9(1)°, with Δ = 22.6° and with an average value = 99.3(1)°. From Table 2 it is noticeable that within the range of τ values of 0.76–0.09, there is slight gap of 0.22 in τ value between the value of 0.54 for 7 to the next value of 0.76 for 8. This gap corresponds with a change in the ratio of the x₀ and x₁₀ angles, for τ values >0.54, x₀ > x₁₀, but for τ values <0.54, x₀ < x₁₀. These relatives have been used to suggest a structural pathway from a regular trigonal bipyramidal to a distorted square-based pyramidal stereochemistry and suggest that, 1–9 form a point in a more extensive structural pathway for the Cu₅N₄ stereochemistry.
Table 1
Crystallographic and structure refinement data for eight [Cu(dpyam)₂(NCO)]Y complexes

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₂₁H₁₈N₇CuOBr</th>
<th>C₂₁H₁₈N₇CuO₂F₃S</th>
<th>C₂₁H₂₁N₁₀CuOBF₄</th>
<th>C₂₁H₂₃N₇CuO₂Cl</th>
<th>C₂₁H₁₈N₇CuO₄</th>
<th>C₂₁H₁₈N₇CuOF₆</th>
<th>C₂₁H₁₈N₇CuO₅Cl</th>
<th>C₂₁H₁₈N₇CuOB</th>
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<tr>
<td>M</td>
<td>527.87</td>
<td>597.03</td>
<td>705.98</td>
<td>555.48</td>
<td>509.97</td>
<td>592.93</td>
<td>547.38</td>
<td>767.22</td>
</tr>
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<td>Crystal system</td>
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<td>orthorhombic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
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<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/n</td>
<td>Pbcn</td>
<td>P₂₁/c</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.9720(1)</td>
<td>15.8752(2)</td>
<td>19.9263(6)</td>
<td>7.1030(3)</td>
<td>11.0911(2)</td>
<td>8.3080(1)</td>
<td>8.1782(6)</td>
<td>13.2229(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>16.5463(1)</td>
<td>16.7884(2)</td>
<td>7.6268(3)</td>
<td>27.9710(2)</td>
<td>16.323(3)</td>
<td>14.0520(2)</td>
<td>10.1466(1)</td>
<td>9.7836(7)</td>
</tr>
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<td>c (Å)</td>
<td>12.0719(1)</td>
<td>18.6085(3)</td>
<td>22.7070(9)</td>
<td>12.6930(8)</td>
<td>11.8435(2)</td>
<td>13.9620(9)</td>
<td>13.9620(9)</td>
<td>29.805(2)</td>
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<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>β (°)</td>
<td>98.492(2)</td>
<td>90</td>
<td>112.410(1)</td>
<td>96.899(3)</td>
<td>99.934</td>
<td>91.061(3)</td>
<td>91.8200(1)</td>
<td>101.8880(1)</td>
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<td>γ (°)</td>
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<td>90</td>
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<td>90</td>
<td>90</td>
<td>90</td>
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<td>90</td>
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<tr>
<td>V (Å³)</td>
<td>2167.6(3)</td>
<td>4959.5(1)</td>
<td>3190.3(2)</td>
<td>2503.6(2)</td>
<td>2112.1(6)</td>
<td>2358.6(6)</td>
<td>2299.3(3)</td>
<td>3773.1(5)</td>
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<td>Z</td>
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<td>8</td>
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<tr>
<td>Dₐ (g cm⁻³)</td>
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<td>1.599</td>
<td>1.470</td>
<td>1.452</td>
<td>1.604</td>
<td>1.670</td>
<td>1.581</td>
<td>1.351</td>
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<tr>
<td>μ (mm⁻¹)</td>
<td>2879</td>
<td>1.032</td>
<td>0.752</td>
<td>1.024</td>
<td>1.083</td>
<td>1.072</td>
<td>1.115</td>
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</tr>
<tr>
<td>F(000)</td>
<td>1060</td>
<td>2424</td>
<td>1444</td>
<td>1116</td>
<td>1044</td>
<td>1196</td>
<td>1116</td>
<td>1596</td>
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<tr>
<td>Crystal size (mm)</td>
<td>0.20 × 0.16 × 0.04</td>
<td>0.38 × 0.28 × 0.25</td>
<td>0.25 × 0.15 × 0.10</td>
<td>0.43 × 0.20 × 0.18</td>
<td>0.15 × 0.12 × 0.06</td>
<td>0.26 × 0.08 × 0.06</td>
<td>0.16 × 0.13 × 0.08</td>
<td>0.39 × 0.19 × 0.13</td>
</tr>
<tr>
<td>Number of reflections collected</td>
<td>18832</td>
<td>33809</td>
<td>22102</td>
<td>8129</td>
<td>11204</td>
<td>20607</td>
<td>14511</td>
<td>32358</td>
</tr>
<tr>
<td>Number of unique reflections (Rint)</td>
<td>5169 (0.0542)</td>
<td>7225 (0.0384)</td>
<td>9087 (0.0804)</td>
<td>3869 (0.0394)</td>
<td>3846 (0.0478)</td>
<td>5657 (0.0572)</td>
<td>5436 (0.0381)</td>
<td>9035 (0.0284)</td>
</tr>
<tr>
<td>Data/restraints/parameter</td>
<td>5169/0/352</td>
<td>7225/0/422</td>
<td>9087/0/582</td>
<td>3869/0/389</td>
<td>3846/0/380</td>
<td>5657/0/461</td>
<td>5436/0/396</td>
<td>9035/0/648</td>
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<tr>
<td>Goodness-of-fit</td>
<td>1.030</td>
<td>1.027</td>
<td>1.010</td>
<td>1.105</td>
<td>1.018</td>
<td>1.029</td>
<td>1.035</td>
<td>1.054</td>
</tr>
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<td>Final R indices</td>
<td>R₁ = 0.0514,</td>
<td>R₁ = 0.0587,</td>
<td>R₁ = 0.0789,</td>
<td>R₁ = 0.0472,</td>
<td>R₁ = 0.0405,</td>
<td>R₁ = 0.0541,</td>
<td>R₁ = 0.0649,</td>
<td>R₁ = 0.0471,</td>
</tr>
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<td>wR₂ = 0.1023,</td>
<td>wR₂ = 0.1493</td>
<td>wR₂ = 0.1010</td>
<td>wR₂ = 0.1318</td>
<td>wR₂ = 0.0884</td>
<td>wR₂ = 0.1065</td>
<td>wR₂ = 0.1611,</td>
<td>wR₂ = 0.1117</td>
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<tr>
<td>R indices (all data)</td>
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<td>R₁ = 0.0827,</td>
<td>R₁ = 0.2686,</td>
<td>R₁ = 0.0768,</td>
<td>R₁ = 0.0583,</td>
<td>R₁ = 0.0944,</td>
<td>R₁ = 0.0966,</td>
<td>R₁ = 0.0636,</td>
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<td>wR₂ = 0.1151,</td>
<td>wR₂ = 0.1662</td>
<td>wR₂ = 0.1453</td>
<td>wR₂ = 0.0957,</td>
<td>wR₂ = 0.1197</td>
<td>wR₂ = 0.1790</td>
<td>wR₂ = 0.1201,</td>
<td>wR₂ = 0.1201</td>
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<tr>
<td>Largest differential peak and hole (e Å³)</td>
<td>0.489, −0.481</td>
<td>0.728, −0.674</td>
<td>0.208, −0.223</td>
<td>0.515, −0.583</td>
<td>0.362, −0.308</td>
<td>0.317, −0.371</td>
<td>0.799, −0.452</td>
<td>0.349, −0.395</td>
</tr>
</tbody>
</table>
3.3. Scatter-plot analysis for the [Cu(dpyam)$_2$(NCO)][Y] series of complexes

This section presents the data for the [Cu(dpyam)$_2$(NCO)][Y] series of complexes, Table 2, using scatter-plot analysis. The scatter plots (Fig. 3) discussed are as follows:

(a) $\tau$ versus Cu–N(4), (b) $x_2$ versus $x_1$, (c) $x_1$ versus Cu–N’ and (d) Cu–N(2) versus Cu–N(4). An overview of the range of stereochemistries is provided by the plot of $\tau$ versus Cu–N(4). However, as $\tau$ involves two simultaneous angle changes, it will not be used further. A number of suggested extreme data points, Table S2, are included in the plots, with the geometry of the extreme seesaw stereochemistry illustrated in Fig. S1. The nine data points in Fig. 3(a) vary from trigonal bipyramidal, TB, to near regular-square-based pyramidal, RSBP, with the $\tau$ values decreasing from 0.76 to 0.09, respectively as the Cu–N(4) distances increase from 2.089(1) to 2.283(3) Å. The data points show a broad inverse trend, and clearly do not cluster around the RTB geometrical point. This plot provides an overview of the observed stereochemistries of the [Cu(dpyam)$_2$(NCO)][Y] series of complexes. There is one data point, 1, at near SBP with $\tau = 0.09$, but there are no data points at RTB ($\tau = 1.0$). Five of the nine data points have $\tau$ values in the range 0.23–0.31 with stereochemistries best described as TBDSBP. Two data points 6 and 7 lie on the main correlation trend-line containing the RTB and RSBP data points. Two data points, 4 and 8 lie on a parallel correlation, with the remaining one data point, 9 lying nearby. Data points 1 and 2 lie off the RTB $\rightarrow$ RSBP trendline, due to their slightly long Cu–N(4) bond distances, which are $\approx$0.1 Å greater than expected [16].

The data points in Fig. 3(b) show the $x_1$ values decreasing from 115.9(1)$^\circ$ to 94.1(2)$^\circ$ as the $x_1$ values concurrently increase from 124.7(2)$^\circ$ to 167.1(1)$^\circ$. All eight data points have $x_1$ values $>$120$^\circ$ and $x_3$ values $<$120$^\circ$. Table 2. Eight data points are found in the $-A + B$ section of the graph. The exception is data point, 1, which lies close to the RSBP reference point. It is noticeable that within the $x_1$ and $x_3$ data set, point 1 has greater $x_1$ and $x_3$ values compared to those of a RSBP stereochemistry. There is no data points, which lies on the RTB $\rightarrow$ RSBP ($-A + B$) distortion pathway. Four data points, 2, 3, 4 and 9, and the SBP data point, show an inverse trend, with each of these data points having $x_2$ 105 ± 2$. The remaining data points, 8, 7 and 5, lie on two possible parallel correlations (-----) displaying $x_2$ values of 120 ± 2$, 115 ± 2$ and 110 ± 1$, respectively. This series of three possible parallel correlations have the same gradients. The data points show a SBP distortion, but only the correlation containing the data points corresponding to an $x_2$ value of 105$^\circ$ can end up at RSBP. For each parallel correlation, the $x_2$ values remain constant, therefore $\Delta x_1 = \Delta x_3 = x_1 + x_3 = 360^\circ$, Table S3, and possibly suggesting the occurrence of preferred or magic angles [19].

The % $-A$ and % $+B$ distortion values calculated from the in-plane $x_1$ and $x_3$ bond angle data of Fig. 3(b) are given in Table 3.
The nine data points in Fig. 3(c) show the $z_3$ values decreasing from 115.9(1)$^\circ$ to 94.1(2)$^\circ$, $\Delta z_3 = 21.8^\circ$ as the Cu–N distances decrease from 1.984(1) to 1.903(13) Å, $\Delta$Cu–N = 0.081Å. All data points have $z_3$ values <120$^\circ$ and Cu–N distances <2.092 Å, suggesting A route distortion. Data point 8 lies well off the $-A \rightarrow$ RTB $\rightarrow +A$ pathway, with Cu–N distances significantly shorter, $\approx$0.08 Å, than predicted from its corresponding $z_3$ values, while data points 1–7 also seem to have slightly shorter Cu–N distances, $\approx$0.05 Å, than expected from their corresponding $z_3$ values. There are no data points connecting the RTB data point to the extreme ‘see saw’ data point (the $-A$ route distortion, SSDTB in Fig. S1) There are two possible higher parallel trend lines involving one data point 8, and two data points 1–7.
points, 2 and 6 with 1, 3, 4, 5 and 7 lying close by. These linear correlations do not have enough data points to be convincing. However, it is significant that the three correlations involve approximately equal separations between the lines of either \( \approx 11^\circ \) in the \( \alpha_3 \) values or of \( \approx 0.040 \) Å in the Cu–N' distances. If the data of Fig. 3(c) are related to those of Fig. 1, then both the \( \alpha_3 \) angles and the Cu–N' distances correspond to a pure \(-A\) route distortion of the RTB stereochemistry. In practice, the \( \alpha_1 \) and \( \alpha_2 \) angles are not even approximately equal, varying from \( \Delta(\alpha_1 - \alpha_2) = 5.3–68.3^\circ \), Table 2. The extreme \(-A\) route distortion is clearly five-coordinate, with three short bonds,
Cu–N(1) = Cu–N(3) ≈ 2.0 Å, Cu–N′ ≈ 1.95 Å, and two longer bonds, Cu–N(2) = Cu–N(4) ≈ 2.15 Å, with in-plane angles of χ1 = χ2 = 135° and χ3 = 90°.

The data points in Fig. 3(d) show the Cu–N(2) distances decreasing from 2.074(2) to 2.014(10) Å, while the Cu–N(4) distances increase from 2.089(1) to 2.283(3) Å. Five data points, 2, 4–7 are observed in the −A + B quadrant of the graph, with points 1, 3, 8 and 9 lying outside this quadrant. There are no data points on the RTB −A trendline, but there is one data point, 3 which lies directly on the RTB → +B route pathway. There are two data points 6 and 7 which also lie precisely on the RTB → RSBP (−A + B) pathway, with data point 2, lying close by. Table 4 shows the % −A and % +B distortion values of the complexes calculated using the in-plane angle data of Fig. 3(b).

3.4. General conclusions and comparison of the \([\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}] \) series with other \([\text{Cu}(\text{chelate})_2(\text{X})][\text{Y}] \) series of complexes

The information obtained from the scatter-plot analysis of this series of nine \([\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}] \) complexes can be summarised as follows:

1. The distribution of the data points is not random, with respect to the RTB and RSBP data points. They involve a significant spread of 42° and 0.19 Å, Table S1.
2. The τ plot is consistent with a SBP distortion of the RTB CuN₂N’ chromophore, but with neither the RTB or RSBP structures present. Data point, 1, has extreme to near RSBP geometry with a τ value of 0.09. Five complexes have τ values in the range of 0.23–0.31. Data points, 6 and 7, have an intermediate τ values of 0.53 and 0.54, respectively. Data point, 8, has an exceptional τ value of 0.76, which equates with an unusual SBPD TB stereochemistry for a \([\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}] \) complex.

The plot of z₃ versus z₁ shows data points lying on parallel correlations, with fixed z₂ values of 120 ± 5°, 10° or 15°, suggesting the existence of preferred or magic angles, consistent with z₁ + z₂ + z₃ = 360°, Table S3.

The ±A and ±B axes of Fig. 1 can be superimposed on the plots. All data points lie in the −A + B section of the graphs except data point 1 which lies close to the RSBP stereochemistry. Tables 3 and 4 show the % −A and % +B distortion values of the complexes calculated from the in-plane angle and distance data and show large % values of both −A and +B distortion.

The five-coordinate structures of the dpyam series are comparable to the five-coordinate copper(II) complexes \([\text{Cu}(\text{chelate})_2(\text{X})][\text{Y}] \) when chelate = bipy and phen and X = Cl⁻, Br⁻, I⁻ and H₂O. Those of the bipy and phen families also show distortions ranging from RTB to RSBP, but differ in two aspects. First, almost all the τ values in the corresponding bipy and phen complexes range between intermediate to near RTB, \([\text{Cu}(\text{phen})_2\text{Cl}][\text{Y}] \) [9a] (0.56–0.81), \([\text{Cu}(\text{phen})_2\text{Br}][\text{Y}] \) [9b] (0.72–0.95), \([\text{Cu}(\text{phen})_2\text{I}][\text{Y}] \) [9b] (0.84–1.06), \([\text{Cu}(\text{bipy})_2\text{Cl}][\text{Y}] \) [3,9d] (0.53–1.00), \([\text{Cu}(\text{bipy})_2\text{Br}][\text{Y}] \) [9b,9d] (0.49–0.91), \([\text{Cu}(\text{bipy})_2\text{I}][\text{Y}] \) [9b] (0.80–0.90) and \([\text{Cu}(\text{chelate})_2(\text{OH}_2)][\text{Y}] \) [9c] (0.53–0.89), which differ significantly from the dpyam complexes of series where most τ values = 0.09–0.54 due to the more flexible dpyam ligand. Secondly, the distortion structural pathway in the dpyam series involves a −A + B route (Fig. 1), which is different from that of the higher symmetry with twofold axis of \([\text{Cu}(\text{chelate})_2(\text{OH}_2)][\text{Y}] \) series which involves, a unique ±A route.

The stereochemistries of the \([\text{Cu}(\text{chelate})_2(\text{OH}_2)][\text{Y}] \) complexes differ from that of the dpyam complexes in having a crystallographic twofold axis of symmetry and hence are best described as having a pure ±A route distortion, which involves the pure υₘₘₙ and υₘₘₙ modes of vibration. The \([\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}] \) complexes in contrast, with their slight contraction along the Cu–N’ distance (opposite z₃), their non-equivalence of the χ₁ and χ₂ angles without a

Table 3
The % −A and % +B route distortion values of the complexes calculated using the in-plane angle data of Fig. 3(b)

<table>
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<tr>
<th>Complex</th>
<th>1</th>
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<tr>
<td>% −A</td>
<td>82.0</td>
<td>77.3</td>
<td>81.2</td>
<td>97.9</td>
<td>71.7</td>
<td>80.0</td>
<td>73.2</td>
<td>15.3</td>
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<tr>
<td>% +B</td>
<td>49.4</td>
<td>85.8</td>
<td>89.6</td>
<td>80.7</td>
<td>83.0</td>
<td>46.1</td>
<td>47.2</td>
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Table 4
The % −A and % +B route distortion values of the complexes calculated using the in-plane distance data of Fig. 3(d)

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<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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</thead>
<tbody>
<tr>
<td>% −A</td>
<td>82.5</td>
<td>7.9</td>
<td>28.6</td>
<td>46.0</td>
<td>38.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% +B</td>
<td>91.8</td>
<td>60.9</td>
<td>76.8</td>
<td>66.5</td>
<td>69.3</td>
<td>45.9</td>
<td>44.0</td>
<td>8.4</td>
</tr>
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</table>
twofold axis of symmetry are considered to involve a 
$-A + B$ route distortion with the obvious domination of 
$+B$ over $-A$, involving all the four modes of vibration 
$v_{sym}^{str}$, $v_{sym}^{str}$ and $v_{sym}^{asym}$, namely the molecular structure 
VI of Fig. 1. Alternatively, the precise coordination geometry displayed may be interpreted [9b] as an effect of vibronic coupling of a linear combination of the nuclear modes of vibrations $v_{sym}$, a symmetric $C_2$ mode, and $v_{asym}$, an asymmetric non-$C_2$ mode, of the CuN₄N’ chromophore.

3.5. IR, electronic properties and EPR of the 
[Cu(dpyam)$_2$(NCO)]$^+$Y complexes

The infrared spectra display a strong band at 2214 and 
2180 cm$^{-1}$ for 1, 2214 cm$^{-1}$ for 2, 2209 cm$^{-1}$ for 3, 
2220 cm$^{-1}$ for 4, 2219 and 2202 cm$^{-1}$ for 5, 2222 cm$^{-1}$ for 
6, 2214 cm$^{-1}$ for 7 and 2218 cm$^{-1}$ for 8, which can be 
assigned to the $v_{asym}$(NCO) absorption band. The spectrum of 2 
also displays a broad and intense band at approximately 
1280–1040 cm$^{-1}$, consistent with the characteristic peak for $v_{asym}$(SO$_3$) of CF$_3$SO$_3^-$ anion. The spectrum of 3 displays a 
broad and intense band at approximately 1074– 
1014 cm$^{-1}$, consistent with the characteristic peak of BF$_3^-$ 
anion. The spectrum of 5 displays an intense band at approximately 1384 and 1307 cm$^{-1}$, consistent with the 
characteristic peak of $v_{asym}$(NO) and $v_{asym}$(NO) of NO$_3^-$ anion. The spectrum of 6 displays a broad and intense band at approximately 845–837 cm$^{-1}$, consistent with the characteristic peak of PF$_3^-$ anion. The spectrum of 7 displays a broad and intense band at approximately 1166–1076 cm$^{-1}$, consistent with the characteristic peak of ClO$_4^-$ anion.

The polycrystalline electronic reflectance spectra of complexes 1, 5, 6 and 8 are represented in Fig. 4. For 8 a single d → d transition occurs at 11420 cm$^{-1}$ (876 nm), with some evidence of an unresolved high-energy shoulder at 12880 cm$^{-1}$ (776 nm), consistent with near TB stereochemistry ($\tau = 0.76$). The one-electron ground-state configuration is $d_{z^2} > d_{y^2} \approx d_{x^2-y^2} > d_{xz} \approx d_{yz}$. The principal absorption may be assigned as a $d_{x^2-y^2} \rightarrow d_{z^2}$ transition, with the low-energy assigned as a $d_{x^2-y^2} \rightarrow d_{yz}$ transition. The electronic spectrum of 8 is comparable to those of complexes with similar Cu(II) environment [Cu(phen)$_2$Br][Y], Y = Br · H$_2$O, ClO$_4$ and PF$_6$ [9b]. The spectra of 6 and 7, $\tau = 0.53$ and 0.54, respectively, both having an intermediate stereochemistry between RTB and RSBP, involve two clearly resolved peaks at 10330 cm$^{-1}$ (968 nm) and 13870 cm$^{-1}$ (721 nm) for 6 and 10350 (966 nm) and 13800 cm$^{-1}$ (725 nm) for 7, with the lower-energy peak showing a slightly greater intensity, consistent with the intermediate five-coordinate geometry. The one-electron ground-state configuration is $d_{z^2} > d_{y^2} > d_{y^2} > d_{x^2} \approx d_{yz}$. The transitions may be assigned as the $d_{y^2} \rightarrow d_{x^2}$ transition for the low-energy peak and the $d_{y^2} \approx d_{y^2} \rightarrow d_{y^2} \rightarrow d_{y^2}$ transition for the high-energy peak. The electronic spectra of 6 and 7 are comparable to those of complex with similar environment [Cu(phen)$_2$Cl][CF$_3$SO$_3$] · H$_2$O [9a]. Complexes 1–5, $\tau = 0.09–0.31$, which have a TBDSBP stereochemistry, involve high-energy, high-intensity peak at 14510 cm$^{-1}$ (689 nm), 14420 cm$^{-1}$ (694 nm), 14240 cm$^{-1}$ (702 nm), 14200 cm$^{-1}$ (704 nm) and 13930 cm$^{-1}$ (718 nm), respectively, with low-energy, low-intensity shoulder at 10150 cm$^{-1}$ (985 nm), 10180 cm$^{-1}$ (982 nm), 10220 cm$^{-1}$ (978 nm), 10350 cm$^{-1}$ (966 nm) and 10270 cm$^{-1}$ (974 nm), respectively. The one-electron ground state configuration is $d_{z^2} > d_{y^2} > d_{y^2} > d_{y^2}$, $d_{y^2} \approx d_{x^2}$, $d_{yz} \approx d_{y^2}$. The transitions may be assigned as the $d_{z^2} \rightarrow d_{y^2}$ transition for the low-energy shoulder and the $d_{y^2} \approx d_{y^2} \rightarrow d_{y^2}$ transition for the high-energy peak.

The electronic spectra of 1–5 are comparable to those of complexes with similar environment [Cu(phen)$_2$Cl][BF$_4$] [9a] and [Cu(phen)$_2$Br][BF$_4$] [9b].

The corresponding spectro-structural correlation plots (Fig. S2) reveal that $\Delta E$ values increase with increasing $\tau$ values for the low-energy peak and the reverse result has been found for the higher-energy peaks. It is evident from Fig. S3, that the basal angles themselves correlate very well with the $\Delta E$ values. This plot clearly indicates that a linear correlation between $\tau$ and the $\Delta E$ values exists in the set of 1–8 where $\alpha$ and $\beta$ have been defined consistently.

The polycrystalline X-band EPR spectrum at room temperature of complexes 1–8 is isotropic (Table 5), yielding no information in relation to the electronic ground state. Low-temperature (77 K) EPR spectra were performed at higher frequencies (K-band and V-band) than X-band, both on polycrystalline samples, and DMSO solutions, in

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<tbody>
<tr>
<td>$g_x$</td>
<td>2.05</td>
<td>2.04</td>
<td>2.05</td>
<td>2.030</td>
<td>2.03</td>
<td>2.05</td>
<td>2.04</td>
<td>2.185</td>
</tr>
<tr>
<td>$g_y$</td>
<td>2.05</td>
<td>2.10</td>
<td>2.08</td>
<td>2.075</td>
<td>2.09</td>
<td>2.13</td>
<td>2.08</td>
<td>2.185</td>
</tr>
<tr>
<td>$g_z$</td>
<td>2.27</td>
<td>2.17</td>
<td>2.28</td>
<td>2.245</td>
<td>2.17</td>
<td>2.20</td>
<td>2.24</td>
<td>2.005</td>
</tr>
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* Estimated error: ±0.01 for samples 4 and 8, ±0.02 for all others.
order to increase the g-value resolution, and possibly also resolve hyperfine structure. Indeed, Q-band (34 GHz) spectra of frozen DMSO solutions showed nicely resolved parallel and perpendicular g components, with a hyperfine structure due to the nuclear $I = 3/2$ spin characteristic for Cu$^{2+}$ observed on top of the parallel component (not shown), this was expected to study the correlation between the five-coordinate geometries and the hyperfine splitting ($A_\parallel$ values). However, an analysis of the solution spectra revealed that the complexes under study are decomposed, or otherwise altered in these conditions. These studies were consequently abandoned. Instead, EPR on polycrystalline samples at K-band (27 GHz) and V-band (54 GHz) was successful in fully resolving g-values. Fig. 5 shows spectra of 4 and 8 at both frequencies, accompanied by powder simulations using g-values as in Table 5. Table 5 also presents g-values for the remaining complexes under study. The EPR spectra of complexes 1–7 are in rhombic type [4,7] and three g-factors are obtained as in Table 5, with the lowest g-values > 2.0 which is consistent with the $d_{Janowski}$ ground state, while the EPR spectrum of complex 8 is axial with $g_\perp = 2.185$ and $g_\parallel = 2.005$, consistent with a $d_{z^2}$ ground state for the approximately trigonal bipyramidal stereochemistry of the CuN$_4$N’ chromophore present, $g_\perp \gg g_\parallel > 2.0$.

4. Conclusions

The present report describes the preparation, crystal structure determination, spectroscopic properties and structural pathway of the five-coordinate copper(II) complexes with pseudohalide ligand, NCO$^-$. The structure of the [Cu(dpyam)$_2$(NCO)]$^+$ cations all involve a five-coordinate CuN$_4$N’ chromophore with TBDSBP in 1–5 and 9 ($\tau = 0.09–0.31$, respectively). Complexes 6 and 7 exhibit an intermediate five-coordinate, slightly distorted toward TBP ($\tau = 0.53$ and 0.54, respectively). The complex 8 shows SBPDTB with a $\tau$ value of 0.76. The detailed structure of a five-coordinate copper(II) complex is dependent upon the type of counter anion in the lattice, due to the ‘Plasticity Effect’, showing how the same complex in different crystal modifications, can have slightly different structures. In the present work the ‘Plasticity Effect’ has been considerably extended by reference to cation distortion isomers, in which the structures of a given cation is modified in the presence of different counter anions. The relatively small structural
differences produced have been correlated to suggest the existence of a continuous 'Structural Pathway', connecting the extreme structures, with the individual structures linked by a soft mode of vibration. All data points are found in the $-A + B$ section of the graph, except a data point 1, which is close to RSBP. It is noticeable that the $a_1$ and $a_3$ of 1 are greater than the usual values of $a_1$ and $a_3$ usually found for RSBP complexes, leading to this deviation. Moreover, this structure is the most extreme RSBP known of five-coordinate with dpyam ligand.

Acknowledgements

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Appendix A. Supplementary material

CCDC numbers 295201, 295202, 295203, 295204, 295205, 295206, 295207 and 295208 contain the supplementary crystallographic data for 1, 2, 3, 4, 5, 6, 7 and 8. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.09.027.

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