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PAPER

Restricting the geometrical relaxation in four-coordinate copper(I) complexes using face-to-face and edge-to-face π-interactions†

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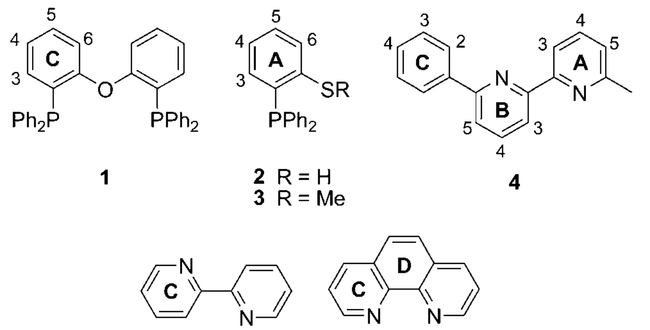
A series of $[Cu(N,N)(P,P)]^+$, $[Cu(N,N)(P,S)]^+$, $[Cu(N,N)_2]^+$ and $[Cu(P,S)_2]^+$ complexes incorporating the ligands 2,2′-bipyridine, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane, bis(2-(diphenylphosphino)phenyl)ether (**1**), 2-diphenylphosphinothioanisole (**3**) and 2-methyl-6′-phenyl-2,2′-bipyridine (**4**) has been synthesized and structurally characterized. We have assessed the degree of distortion of two bidentate ligands away from an ideal tetrahedral arrangement about the copper(I) ion using the White model. The greatest distortion along a pathway towards square planar coordination is observed in $[Cu(4)_2][PF_6]$ and is a result of intra-cation π-stacking between phenyl and bpy domains. Each of the complexes which contain the *P*,*S*-chelating ligand 3 exhibits significant 'rocking' or 'wagging' distortions which are associated with intra-cation $CH_{methyl}\cdots\pi$ interactions. The extent of this distortion can also be assessed using a less rigorous approach by measuring the S–Cu–X and P–Cu–X angles where the S and P atoms belong to ligand 3, and X is the midpoint of the backbone of the second ligand. $[Cu(3)_2][PF_6]$ and $[Cu(1)(3)][PF_6]$ exhibit embraces between the phenyl substituents that result in the copper(I) ion being sterically protected, and the room temperature ^1H NMR solution spectrum of $[Cu(1)(3)][PF_6]$ reveals hindered rotation of the phenyl rings of ligand.

Introduction

We are currently interested in the development of derivatives of earth-abundant metals for use in energy applications and have demonstrated that efficient dye-sensitized solar cells (DSCs) can be fabricated using bis(2,2′-bipyridine) copper(I) complexes.[1] In conjunction with further studies of copper(I) complexes for this application,[2,3] we have been exploring the more general use of complexes of earth abundant elements for incorporation as emitters in light-emitting electrochemical cells (LECs). The emission properties of copper(I) complexes containing a combination of hard *N*,*N*- and soft *P*,*P*-chelates have been the focus of a number of studies over the last few years.[4–9] The combination of an *N*,*N*-donor set (*e.g.* bpy or phen derivatives, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) with a soft donor set (notably chelating bis(phosphines)) enhances emission behaviour with respect to the $[Cu(N,N)_2]^+$ complexes. Particularly noteworthy are $[Cu(2,9\text{-}Me_2phen)(\mathbf{1})]^+$ and $[Cu(2,9\text{-}^nBu_2phen)(\mathbf{1})]^+$ (2,9-Me_2phen = 2,9-dimethyl-1,10-phenanthroline, 2,9-$^nBu_2$-phen = 2,9-di-*n*-butyl-1,10-phenanthroline, and **1** is shown in Scheme 1) which exhibit emissions at 570 and 560 nm, respectively (in CH_2Cl_2) with quantum yields of 0.15 and 0.16, and lifetimes of 14.3 and 16.1 μs.[4] Armaroli and coworkers have reported strongly luminescent $[Cu(N,N)(P,P)]^+$ complexes in which *P*,*P* is ligand **1**, and *N*,*N* is a 2,9-disubstituted or 2,4,7,9-tetrasubstituted phen ligand and demonstrated moderate efficiency for a LEC device incorporating $[Cu(2,9\text{-}^nBu_2phen)(\mathbf{1})]^+$.[5] The formation of dinuclear $[Cu_2(N,N)_2(\mu\text{-}P,P)_2]^{2+}$ complexes may compete with $[Cu(N,N)(P,P)]^+$ species.[10,11] Most of the above examples demonstrate that the presence of sterically demanding substituents in the *N*,*N*-ligand militate against emission quenching by suppressing geometric relaxation and donor solvent association of the excited state complex. Nonetheless, these substituents are not essential for luminescent



Scheme 1 Structures of ligands with numbering scheme used for NMR spectroscopic assignments; unsubstituted Ph rings are labelled **B** in **2**, **3** and dppe, and **D** in **1**.

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behaviour.[10] It should also be noted that flattening distortions of the copper(I) coordination sphere are also constrained by the effects of the crystal matrix.[12]

Since there are many advantages to incorporating simple ligands into complexes that may ultimately be used in the production of devices, we decided to screen a series of $[Cu(N,N)(P,P)]^+$, $[Cu(N,N)(P,S)]^+$, $[Cu(N,N)_2]^+$ and $[Cu(P,S)_2]^+$ complexes in which the interligand interactions should protect the copper(I) centre and minimize geometric relaxation of the excited state. We note that although the preparation of air-stable copper(I) complexes with 2,2′-bipyridine ligands typically requires the presence of substituents at the 6- and 6′-positions,[13] the complex [Cu(phen)(**1**)][BF_4] has been isolated and structurally characterized,[8] indicating that the presence of a substituent 'umbrella' is not essential. Perhaps surprisingly, the range of $[Cu(N,N)(P,P)]^+$ cations studied to date is limited, and the extension of the soft donor set to *P*,*S*-chelates such as **2** and **3** (Scheme 1) is little explored. In this paper, we present the syntheses, and solution and solid-state characterization of a series of homo- and heteroleptic bis(bidentate) copper(I) complexes. Our aim is to screen a series of complexes focusing on their solid state structures and the manner in which the ligands envelop the copper(I) centre in each complex. For optimal oxidative and photophysical stability, future studies will concentrate on complexes possessing substituents *ortho* to the nitrogen donors.

Experimental

General

NMR spectra were recorded at room temperature on a Bruker Avance DRX-500 spectrometer; ^{1}H and ^{13}C chemical shifts are relative to residual solvent peaks (TMS δ 0 ppm), and ^{31}P are referenced to 85% aqueous H_3PO_4. IR spectra (solid samples on a Golden Gate diamond ATR accessory) were recorded on a Shimadzu FTIR-8400S spectrophotometer. Electrospray ionization (ESI) mass spectra were recorded using a Finnigan MAT LCQ or a Bruker esquire 3000^{plus} instrument. A Varian-Cary 5000 spectrophotometer and a Shimadzu RF-5301 PC spectrofluorometer were used, respectively, to record the electronic absorption and emission spectra. Solvents were distilled before use.

2,2′-Bipyridine, 1,10-phenanthroline and ligand **1** were used as received from Acros or Merck. Compounds **2**,[14] **3**,[15] and [Cu(NCMe)$_4$][PF_6][16] were prepared by literature methods. [Cu(6-Phbpy)$_2$][PF_6] was prepared in a similar manner to the literature procedure[17] but using CH_2Cl_2 as a solvent in place of MeCN. [Cu(dppe)$_2$][PF_6] was prepared in an analogous manner to related complexes.[18]

[Cu(bpy)(dppe)][PF$_6$]

[Cu(NCMe)$_4$][PF_6] (93.2 mg, 0.250 mmol) was dissolved in CH_2Cl_2 (50 ml). 1,2-Bis(diphenylphosphino)ethane (99.6 mg, 0.250 mmol) was added to the solution and the reaction mixture was stirred for 2 h at room temperature. Upon the addition of bpy (39.1 mg, 0.250 mmol), the colourless solution turned dark red. The mixture was stirred for 4 h, during which time it turned yellow. Solvent was removed *in vacuo* and the yellow residue was dissolved in CH_2Cl_2, precipitated with Et_2O and separated by filtration. The solid was redissolved in CH_2Cl_2 and the solution was overlaid with Et_2O. Yellow crystals formed overnight. After recovery by filtration, the crystals were dissolved in MeCN and the solution overlaid with Et_2O and left overnight. Yellow crystals of [Cu(bpy)(dppe)][PF_6] formed, were collected by filtration and were washed with Et_2O (131 mg, 0.172 mmol, 68.8%). ^{1}H NMR (500 MHz, $CDCl_3$) (ring B = dppe, ring C = bpy): δ/ppm = 8.52 (d, J = 7.9 Hz, 2H, H^{C3}), 8.31 (d, J = 4.2 Hz, 2H, H^{C6}), 8.13 (t, J = 7.4 Hz, 2H, H^{C4}), 7.47 (m, 2H, H^{C5}), 7.34 (overlapping m, 16H, H$^{B2/B3}$), 7.16 (m, 4H, H^{B4}), 2.62 (m, 4H, H^{CH2}); ^{13}C NMR (126 MHz, $CDCl_3$) δ/ppm = 152.3 (C^{C2}), 150.0 (C^{C6}), 139.5 (C^{C4}), 132.3 (t, J_{PC} = 8 Hz, C$^{B2/B3}$), 130.9 (C^{B4}), 129.6 (t, J_{PC} = 5 Hz, C$^{B2/B3}$), 129.3 (C^{D1}), 126.3 (C^{C5}), 123.2 (C^{C3}), 25.6 (C^{CH2}); ^{31}P NMR (202 MHz, $CDCl_3$) δ/ppm = −4.4 (dppe), −143.6 (septet, J_{PF} = 707 Hz, [PF_6]$^-$); IR (solid): ν/cm^{-1} = 3059 w, 2363 m, 1744 w, 1595 w, 1481 w, 1470 w, 1435 m, 1312 w, 1159 w, 1099 m, 831 s, 762 m, 735 m, 690 s, 667 m, 646 w, 611 w, 555 s, 511 s, 492 s; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 229 (36 300), 294 (21 500), 408 nm (2150 dm^3 mol^{-1} cm^{-1}); emission (CH_2Cl_2 λ_{exc} = 280 nm): λ_{max} = 331, 657 nm. ESI-MS: *m*/*z* 617.0 [M − PF_6]$^+$ (calcd 617.1). Elemental analysis calcd (%) for $C_{36}H_{32}CuF_6N_2P_3$: C 56.66, H 4.23, N 3.67; found: C 56.40, H 4.38, N 3.86.

[Cu(phen)(dppe)][PF$_6$]

[Cu(NCMe)$_4$][PF_6] (93.2 mg, 0.250 mmol) was dissolved in CH_2Cl_2 (50 ml). The ligand dppe (99.6 mg, 0.250 mmol) was added and the colourless solution was stirred for 2 h at room temperature. Addition of phen·H_2O (49.6 mg, 0.250 mmol) caused the solution to turn yellow. The mixture was stirred for 4 h and then solvent was removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2, precipitated with Et_2O, collected by filtration, and washed with Et_2O. [Cu(phen)(dppe)][PF_6] was isolated as a yellow solid (185 mg, 0.235 mmol, 94.0%). ^{1}H NMR (500 MHz, DMSO-d$_6$) (ring B = dppe, rings C = phen): δ/ppm = 8.96 (d, J = 4.5 Hz, 2H, H^{C2}), 8.89 (d, J = 8.1 Hz, 2H, H^{C4}), 8.32 (s, 2H, H^{C5}), 8.06 (dd, J = 8.1, 4.8 Hz, 2H, H^{C4}), 7.43 (m, 2H, H$^{D2+D3+D4}$), 2.78 (m, 4H, H^{CH2}); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ/ppm = 150.6 (C^{C2}), 143.1 (C^{C1a}), 138.1 (C^{C4}), 132.4 (overlapping doublet, C^{B1}), 132.2 (t, J_{PC} = 8 Hz, C$^{B2/B3}$), 130.4 (C^{B4}), 129.5 (C^{C4a}), 129.2 (t, J_{PC} = 5 Hz, C$^{B2/B3}$), 127.3 (C^{C5}), 125.4 (C^{C3}), 24.7 (t, J_{PC} = 20 Hz, C^{CH2}); ^{31}P NMR (202 MHz, DMSO-d$_6$) δ/ppm = −3.2 (dppe), −143.2 (septet, J_{PF} = 707 Hz, [PF_6]$^-$); IR (solid): ν/cm^{-1} = 3100 w, 1680 w, 1653 w, 1558 w, 1435 w, 1101 w, 835 s, 729 m, 694 m, 557 m; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 229 (49 000), 267 (61 100), 420 nm (1500 dm^3 mol^{-1} cm^{-1}); emission (CH_2Cl_2 λ_{exc} = 322 nm): λ_{max} = 370, 428sh nm. ESI-MS: *m*/*z* 640.9 [M − PF_6]$^+$ (calcd 641.1). Elemental analysis calcd (%) for $C_{38}H_{32}CuF_6N_2P_3$·½H_2O: C 57.33, H 4.18, N 3.52; found: C 57.08, H 4.20, N 3.82.

[Cu(3)$_2$][PF$_6$]

[Cu(NCMe)$_4$][PF_6] (93.2 mg, 0.250 mmol) was dissolved in CH_2Cl_2 (50 ml) and ligand **3** (154 mg, 0.500 mmol) was added. The colourless solution was stirred for 2 h at room temperature. Solvent was removed *in vacuo*, and the resulting white solid was dissolved in CH_2Cl_2, precipitated with Et_2O and separated by filtration. After washing with Et_2O, [Cu(**3**)$_2$][PF_6] was isolated as a white solid (158 mg, 0.192 mmol, 76.8%). ^{1}H NMR (500 MHz, CD_3CN): δ/ppm = 7.66 (d, J = 7.9 Hz, 2H, H^{A6}), 7.57 (t, J = 7.6 Hz, 2H, H^{A5}), 7.47 (t, J = 7.4 Hz, 4H, H^{B4}), 7.35 (m, 10H, H^{A4+B3}), 7.22 (br, 8H, H^{B2}), 7.14 (d, J = 7.4 Hz, 2H, H^{A3}), 2.27 (s, 6H, H^{Me}); ^{13}C NMR (126 MHz, CD_3CN) δ/ppm = 143.6 (d, $J_{PC} \approx 20$ Hz, C^{A1}), 135.2 (C^{A3}), 134.7 (C^{A2}, overlapping signal), 134.2 (d, J_{PC} = 6 Hz, C^{B2}), 133.0 (C^{A5}), 132.2 (d, J_{PC} = 25 Hz, C^{B1}), 131.6 (C^{B4+A6}), 130.2 (C^{B3}), 129.1 (C^{A4}), 21.6 (C^{Me}); ^{31}P NMR (202 MHz, $CDCl_3$) δ/ppm = −0.45 (ligand **3**), −143.2 (septet, J_{PF} = 707 Hz, $[PF_6]^-$). IR (solid): ν/cm^{-1} = 3055 w, 1653 w, 1558 w, 1481 w, 1452 w, 1435 m, 1259 w, 1097 m, 1038 w, 970 w, 879 m, 833 s, 743 s, 692 s, 555 s. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 229 (44 100), 265 nm (23 300 dm^3 mol^{-1} cm^{-1}). ESI-MS: *m*/*z* 678.9 [M − PF_6]$^+$ (calcd 679.1). Elemental analysis calcd (%) for $C_{38}H_{34}CuF_6P_3S_2$: C 55.30, H 4.15; found: C 54.94, H 4.26.

[Cu(1)(3)][PF$_6$]

[Cu(NCMe)$_4$][PF_6] (46.6 mg, 0.125 mmol) was dissolved in CH_2Cl_2 (25 ml) and ligand **1** (67.3 mg, 0.125 mmol) was added. The colourless solution was stirred for 2 h at room temperature, after which time ligand **3** (38.5 mg, 0.125 mmol) was added. The solution remained colourless. It was stirred for 4 h and then solvent was removed *in vacuo*. The white solid was dissolved in CH_2Cl_2, precipitated with Et_2O and separated by filtration. After washing with Et_2O, [Cu(**1**)(**3**)][PF_6] was isolated as a white solid (112 mg, 0.106 mmol, 85.0%). ^{1}H NMR (500 MHz, DMSO-d$_6$, see text): δ/ppm = 7.75 (m, 1H, H^{A6}), 7.71 (t, J = 7.6 Hz, 1H, H^{A5}), 7.47 (m, 2H, H^{C5}), 7.42 (overlapping d, J = 8.0 Hz, 1H, H^{A3}), 7.38 (t, J = 7.4 Hz, 2H, H^{B4}), 7.3 (v br, H^D), 7.21 (d, J = 7.5 Hz, 2H, H^{C6}), 7.12 (t, J = 7.1 Hz, 4H, H^{B3}), 7.08 (t, J = 7.4 Hz, 2H, H^{C4}), 6.93 (t, J = 7.3 Hz, 1H, H^{A4}), 6.77 (m, 4H, H^{B2}), 6.7 (v br, H^D), 6.48 (br, 2H, H^{C3}), 2.00 (s, 3H, H^{Me}); ^{13}C NMR (126 MHz, DMSO-d$_6$) δ/ppm = 157.5 (C^{C1}), 142.3 (C^{A1}), 134.0 (C^{C3}), 133.4 (C^{A4}), 132.9 (C^{C5}), 132.3 (C^{A5}), 132.2 (C^{B2+A2}), 130.6 (C^{B4+A3}), 130.1 (C^{B1}), 129.0 (C^{B3}), 128.2 (C^{A6}), 125.5 (C^{C4}), 122.4 (C^{C2}), 120.7 (C^{C6}), 18.7 (C^{Me}) (ring D not assigned); ^{31}P NMR (202 MHz, DMSO-d$_6$) δ/ppm = −2.1 (t, J_{PP} = 64 Hz, ligand **3**), −8.8 (d, J_{PP} = 63 Hz, ligand **1**), −143.2 (septet, J_{PF} = 707 Hz, $[PF_6]^-$). IR (solid): ν/cm^{-1} = 3051 w, 1558 w, 1481 w, 1464 w, 1435 m, 1215 m, 1095 w, 1068 w, 878 w, 833 s, 741 m, 692 s, 557 m. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 232 (47 800), 268 nm (28 000 dm^3 mol^{-1} cm^{-1}); emission (CH_2Cl_2 λ_{exc} = 296 nm): λ_{max} = 330, 438, 650 nm. ESI-MS: *m*/*z* 908.7 [M − PF_6]$^+$ (calcd 909.2), 601.2 [M − PF_6 − **3**]$^+$ (calcd 601.1). Elemental analysis calcd (%) for $C_{55}H_{45}CuF_6OP_4S$: C 62.59, H 4.30; found: C 62.21, H 4.30.

[Cu(bpy)(3)][PF$_6$]

[Cu(NCMe)$_4$][PF_6] (46.6 mg, 0.125 mmol) was dissolved in CH_2Cl_2 (25 ml) and ligand **3** (38.6 mg, 0.125 mmol) was added. The reaction mixture was stirred for 2 h. To the colourless solution, bpy (19.5 mg, 0.125 mmol) was added and the mixture was stirred for 3.5 h during which time a colour change from red to yellow was observed. The solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2. The products were precipitated with Et_2O, but attempts to separate them were unsuccessful. Recrystallization from CH_2Cl_2 layered with Et_2O gave a small number of X-ray quality yellow crystals of [Cu(bpy)(**3**)][PF_6] (see text) and a few red crystals. The yields of the products were too low to allow characterization of the bulk samples.

[Cu(phen)(3)][PF$_6$]

[Cu(NCMe)$_4$][PF_6] (93.2 mg, 0.250 mmol) was dissolved in CH_2Cl_2 (50 ml) and ligand **3** (77.1 mg, 0.250 mmol) was added. The reaction mixture was stirred for 2 h under argon at room temperature. After the addition of phen (49.6 mg, 0.250 mmol), the yellow solution was stirred for 4 h under argon. The mixture was filtered and the solvent was removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 and the solution was filtered. [Cu(phen)(**3**)][PF_6] was precipitated from the filtrate with Et_2O, separated by filtration, washed with Et_2O and isolated as a yellow solid (154 mg, 0.221 mmol, 88.4%). ^{1}H NMR (500 MHz, CD_3CN) (rings C = phen): δ/ppm = 8.89 (br, 2H, H^{C2}), 8.68 (br d, J = 7.2 Hz, 2H, H^{C4}), 8.13 (s, 2H, H^{C5}), 7.91 (m, 3H, $H^{C3+A3/A6}$), 7.65 (t, J = 7.6 Hz, 1H, $H^{A4/A5}$), 7.54–7.30 (overlapping m, 12H, $H^{ring\ B+A3/A6+A4/A5}$), 2.50 (s, 3H, H^{Me}); ^{13}C NMR (126 MHz, CD_3CN) δ/ppm = 151.2 (C^{C2}), 144.2 (C^{A1}), 139.2 (C^{C4}), 135.6 ($C^{A3/A6}$), 133.9 (d, J_{PC} = 16 Hz, $C^{B2/B3}$), 133.4 ($C^{A3/A6}$), 133.2 ($C^{A4/A5}$), 131.6 (C^{B4}), 130.2 (d, J_{PC} = 9 Hz, $C^{B2/B3}$), 128.1 (C^{C5}), 126.4 (C^{C3}), 22.8 (C^{Me}), signals for $C^{A4/A5}$, C^{1a}, C^{4a}, C^{A2} not resolved; ^{31}P NMR (202 MHz, CD_3CN) δ/ppm = −2.1 (ligand **3**), −143.1 (septet, J_{PF} = 707 Hz, $[PF_6]^-$); IR (solid): ν/cm^{-1} = 3100 w, 1558 w, 1506 w, 1423 m, 1095 w, 831 s, 744 m, 723 s, 692 s, 555 s. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 231 (32 900), 234 (31 400), 267 (30 700), 269 (30 600), 394 nm (4400 dm^3 mol^{-1} cm^{-1}); emission (CH_2Cl_2 λ_{exc} = 316 nm): λ_{max} = 350, 688 nm. ESI-MS: *m*/*z* 550.9 [M − PF_6]$^+$ (calcd 551.1). Elemental analysis calcd (%) for $C_{31}H_{25}CuF_6N_2P_2S \cdot \frac{1}{2}H_2O$: C 52.73, H 3.71, N 3.97; found: C 52.84, H 3.70, N 3.97.

[Cu(4)$_2$][PF$_6$]

[Cu(NCMe)$_4$][PF_6] (93.2 mg, 0.250 mmol) was dissolved in CH_2Cl_2 (50 ml) and ligand **4** (186 mg, 0.500 mmol) was added. The dark red solution was stirred for 40 min at room temperature, and then solvent was removed *in vacuo*. The dark red residue was dissolved in CH_2Cl_2, and Et_2O was added to precipitate the product which was collected by filtration. [Cu(**4**)$_2$][PF_6] was isolated as a dark red solid (169 mg, 0.241 mmol, 96.4%). ^{1}H NMR (500 MHz, CD_3CN): δ/ppm = 8.08 (d, J = 8.0 Hz, 2H, H^{A3}), 8.04 (d, J = 8.0 Hz, 2H, H^{B3}), 7.98 (overlapping t, J = 7.8 Hz, 2H, H^{B4}), 7.97 (overlapping t, J = 7.8 Hz, 2H, H^{A4}), 7.57 (d, J = 7.7 Hz, 2H, H^{B5}), 7.47 (d, J = 7.7 Hz, 2H, H^{A5}), 7.26 (d, J = 7.5 Hz, 4H, H^{C2}), 7.00 (t, J = 7.4 Hz, 2H, H^{C4}), 6.77 (t, J = 7.5 Hz, 4H, H^{C3}), 2.32 (s, 6H, H^{Me}); ^{13}C NMR (126 MHz, CD_3CN) δ/ppm = 158.8 (C^{B6}), 157.8 (C^{A6}), 153.6 ($C^{A2/B2}$), 152.6 ($C^{A2/B2}$), 140.2 (C^{C1}), 139.2 ($C^{A4/B4}$), 138.9 ($C^{A4/B4}$), 129.6 (C^{C4}), 128.3 (C^{C3}), 128.2 (C^{C2}), 126.7 (C^{A5}), 125.7 (C^{B5}), 121.6 (C^{B3}), 120.6 (C^{A3}), 25.6 (C^{Me}); IR (solid): ν/cm^{-1} = 3049 w, 2358 m, 1739 w, 1602 w, 1591 w, 1564 m, 1471 m, 1448 m, 1384 m, 1240 m, 1174 m, 1076 w, 921 w, 877 w, 833 s, 786 m, 759 s, 696 s, 640 m, 555 s; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 232 (42 100), 268 (32 300), 307 (33 800), 453 (5800), 536 nm (3900 dm^3 mol^{-1} cm^{-1}); emission (CH_2Cl_2 λ_{exc} = 255 nm): λ_{max} = 425 nm; ESI-MS: *m*/*z* 554.9 [M − PF_6]$^+$ (calcd 555.2). Elemental analysis calcd

(%) for $C_{34}H_{28}CuF_6N_4P$: C 58.25, H 4.03, N 7.99; found: C 57.89, H 4.15, N 8.04.

Crystal structure determinations

Data were collected on a Stoe IPDS instrument; data reduction, solution and refinement used Stoe IPDS software[19] and SHELXL97.[20] Ortep figures were drawn with the program Ortep-3 for Windows.[21] Structures were analysed using Mercury v. 2.3.[22,23]

2{[Cu(bpy)(dppe)][PF$_6$]}·Et$_2$O·1.5CH$_2$Cl$_2$

$C_{77.5}H_{77}Cl_3Cu_2F_{12}N_4OP_6$, M = 1727.70, yellow block, triclinic, space group $P\bar{1}$, a = 11.611(2), b = 13.045(3), c = 14.699(3) Å, α = 115.99(3), β = 97.55(3), γ = 90.93(3)°, U = 1977.1(9) Å^3, Z = 1, D_c = 1.451 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.836 mm^{-1}, T = 173 K, 53 834 reflections collected (12 473 unique), merging r = 0.048. Refinement of 11 793 reflections (488 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0430 ($R1$ all data = 0.0454), w$R2$ = 0.1161 (w$R2$ all data = 0.1179), gof = 1.072.

2{[Cu(phen)(dppe)][PF$_6$]}·Et$_2$O·CH$_2$Cl$_2$

$C_{81}H_{76}Cl_2Cu_2F_{12}N_4OP_6$, M = 1733.28, yellow block, triclinic, space group $P\bar{1}$, a = 11.5635(17), b = 13.0399(17), c = 15.119(2) Å, α = 112.413(10), β = 98.097(11), γ = 91.294(11)°, U = 2079.2(5) Å^3, Z = 1, D_c = 1.384 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.764 mm^{-1}, T = 173 K, 41 833 reflections collected (7716 unique), merging r = 0.059. Refinement of 6781 reflections (507 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0515 ($R1$ all data = 0.0615), w$R2$ = 0.1260 (w$R2$ all data = 0.1316), gof = 1.138.

Compound 6

$C_{36}H_{28}O_2P_2S_2$, M = 618.66, yellow block, monoclinic, space group $C2/c$, a = 16.763(3), b = 5.9420(12), c = 30.238(6) Å, β = 93.51(3)°, U = 3006.3(10) Å^3, Z = 4, D_c = 1.367 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.317 mm^{-1}, T = 173 K, 24 155 reflections collected (3760 unique), merging r = 0.046. Refinement of 3464 reflections (190 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0328 ($R1$ all data = 0.0367), w$R2$ = 0.0824 (w$R2$ all data = 0.0854), gof = 1.096.

[Cu(3)$_2$][PF$_6$]

$C_{38}H_{34}CuF_6P_3S_2$, M = 825.25, colourless block, triclinic, space group $P\bar{1}$, a = 12.137(2), b = 13.453(2), c = 13.9427(19) Å, α = 97.305(12), β = 110.279(12), γ = 114.695(11)°, U = 1838.7(5) Å^3, Z = 2, D_c = 1.491 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.896 mm^{-1}, T = 173 K, 65 210 reflections collected (11 608 unique), merging r = 0.042. Refinement of 11 278 reflections (508 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0284 ($R1$ all data = 0.0293), w$R2$ = 0.0741 (w$R2$ all data = 0.0746), gof = 1.069.

[Cu(1)(3)][PF$_6$]

$C_{55}H_{45}CuF_6OP_4S$, M = 1055.41, colourless block, monoclinic, space group $P2_1/n$, a = 11.476(2), b = 26.337(5), c = 16.155(3) Å, β = 92.18(3)°, U = 4879.2(17) Å^3, Z = 4, D_c = 1.437 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.685 mm^{-1}, T = 173 K, 70 500 reflections collected (9533 unique), merging r = 0.064. Refinement of 9284 reflections (679 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0581 ($R1$ all data = 0.0594), w$R2$ = 0.1241 (w$R2$ all data = 0.1248), gof = 1.225.

[Cu(bpy)(3)][PF$_6$]

$C_{29}H_{25}CuF_6N_2P_2S$, M = 673.07, yellow block, monoclinic, space group $P2_1/n$, a = 10.4500(14), b = 19.688(4), c = 13.830(2) Å, β = 90.245(11)°, U = 2845.3(8) Å^3, Z = 4, D_c = 1.571 Mg m^{-3}, μ(Mo-K$_\alpha$) = 1.016 mm^{-1}, T = 173 K, 44 421 reflections collected (6200 unique), merging r = 0.048. Refinement of 5859 reflections (371 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0341 ($R1$ all data = 0.0365), w$R2$ = 0.0826 (w$R2$ all data = 0.0840), gof = 1.071.

[Cu(phen)(3)][PF$_6$]·CH$_2$Cl$_2$

$C_{32}H_{27}Cl_2CuF_6N_2P_2S$, M = 782.00, yellow block, triclinic, space group $P\bar{1}$, a = 8.9997(16), b = 11.507(2), c = 16.728(4) Å, α = 78.417(16), β = 86.517(16), γ = 78.320(15)°, U = 1661.6(6) Å^3, Z = 2, D_c = 1.563 Mg m^{-3}, μ(Mo-K$_\alpha$) = 1.038 mm^{-1}, T = 173 K, 24 092 reflections collected (6500 unique), merging r = 0.043. Refinement of 5690 reflections (416 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0365 ($R1$ all data = 0.0456), w$R2$ = 0.0745 (w$R2$ all data = 0.0776), gof = 1.126.

[Cu(4)$_2$][PF$_6$]

$C_{34}H_{28}CuF_6N_4P$, M = 701.12, red block, triclinic, space group $P\bar{1}$, a = 10.5396(10), b = 12.2287(10), c = 13.3195(11) Å, α = 104.793(7), β = 102.457(7), γ = 105.796(7)°, U = 1520.2(2) Å^3, Z = 2, D_c = 1.532 Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.840 mm^{-1}, T = 173 K, 44 176 reflections collected (7306 unique), merging r = 0.039. Refinement of 6713 reflections (471 parameters) with $I > 2.0\sigma(I)$ converged at final $R1$ = 0.0362 ($R1$ all data = 0.0408), w$R2$ = 0.0841 (w$R2$ all data = 0.0863), gof = 1.115.

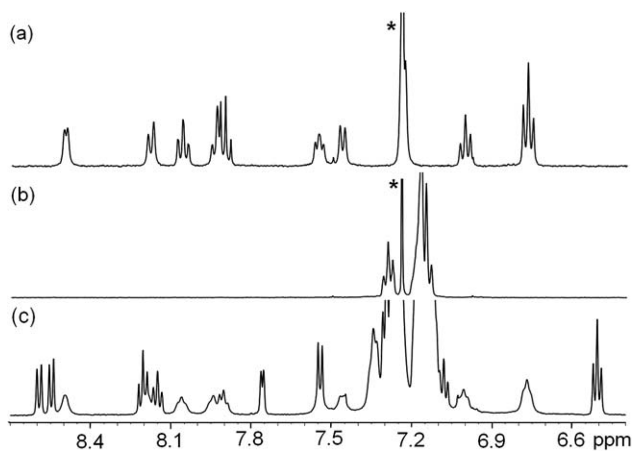


Fig. 1 400 MHz ^{1}H NMR spectra (CDCl$_3$) of (a) [Cu(6-Phbpy)$_2$][PF$_6$] (0.75 × 10^{-5} mol dm^{-3}), (b) [Cu(dppe)$_2$][PF$_6$] (0.75 × 10^{-5} mol dm^{-3}) and (c) equilibrated mixture of [Cu(6-Phbpy)$_2$][PF$_6$] and [Cu(dppe)$_2$][PF$_6$] (each initial solution was 0.75 × 10^{-5} mol dm^{-3}) (* = residual CHCl$_3$).

Results and discussion

Synthetic strategy for heteroleptic complexes

The strategy for the formation of heteroleptic [Cu(*N*,*N*)(*P*,*P*)]$^+$ and [Cu(*N*,*N*)(*P*,*S*)]$^+$ complexes is predicated upon these species being favoured in solution over the respective homoleptic complexes. This was initially demonstrated by comparing the ^{1}H NMR spectra of the homoleptic complexes [Cu(dppe)$_2$][PF$_6$] and [Cu(6-Phbpy)$_2$][PF$_6$] (dppe = 1,2-bis(diphenylphosphino)ethane, 6-Phbpy = 6-phenyl-2,2′-bipyridine) with that of a mixture of the two complexes in $CDCl_3$ which was allowed to equilibrate over a period of a day (Fig. 1). After this time, the ^{1}H and COSY NMR spectra were consistent with the dominant species in solution being [Cu(6-Phbpy)(dppe)][PF$_6$]. Although for this combination of ligands, complete transformation to the heteroleptic species was not achieved, the experiment established the principle that heteroleptic copper(I) complexes could be readily accessed by ligand exchange.

[Cu(bpy)(dppe)]$^+$ and [Cu(phen)(dppe)]$^+$

We began our study with the preparation of salts of [Cu(bpy)(dppe)]$^+$ and [Cu(phen)(dppe)]$^+$. Equimolar amounts of [Cu(NCMe)$_4$][PF$_6$] and dppe were combined in CH_2Cl_2 and after a period of 2 hours at room temperature, one equivalent of either bpy or phen was added. After work up, [Cu(bpy)(dppe)][PF$_6$] and [Cu(phen)(dppe)][PF$_6$] were isolated as yellow crystalline solids in 69 and 94% yields, respectively. The highest mass peaks in the electrospray mass spectra of the complexes appeared at 617.0 (*N*,*N* = bpy) and 640.9 (*N*,*N* = phen) and were assigned to [M − PF$_6$]$^+$. The isotope patterns observed corresponded to those calculated. The complexes were characterized in solution by ^{1}H, ^{13}C and ^{31}P NMR spectra, the former two being assigned using routine 2D techniques (see Experimental section).

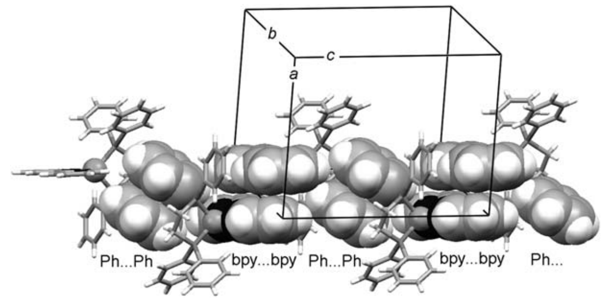


Fig. 3 Packing of [Cu(bpy)(dppe)]$^+$ cations in 2{[Cu(bpy)(dppe)][PF$_6$]}·Et$_2$O·1.5CH$_2$Cl$_2$ showing the face-to-face π-interactions.

Crystals of 2{[Cu(bpy)(dppe)][PF$_6$]}·Et$_2$O·1.5CH$_2$Cl$_2$ suitable for X-ray diffraction grew within a few days from a CH_2Cl_2 solution of the complex layered with Et_2O. The structure of the [Cu(bpy)(dppe)]$^+$ cation is depicted in Fig. 2. Metrical parameters (see figure caption) in the cation are unexceptional, and the angle between the N1Cu1N2 and P1Cu1P2 planes is 84.27(6)°. The asymmetric unit contains 0.75 of a CH_2Cl_2 molecule and 0.50 of a disordered Et_2O molecule, and the remaining part of the latter is generated by symmetry. Cations assemble into rows running parallel to the *c*-axis (Fig. 3) with face-to-face π-interactions[24] between pairs of bpy ligands and pairs of phenyl substituents (the rings containing C1 and C1^i, symmetry code $i = 2 - x, 1 - y, 1 - z$). Close approach of adjacent rows is prevented by the spatial requirements of the PPh$_2$ groups containing P2. This leads to cavities between pairs of bpy ligands containing atoms N1 and N1^{ii} (symmetry code $ii = 1 - x, 1 - y, -z$), each occupied by a disordered Et_2O molecule.

X-Ray quality crystals of 2{[Cu(phen)(dppe)][PF$_6$]}·Et$_2$O·CH$_2$Cl$_2$ were grown overnight from a CH_2Cl_2 solution of [Cu(phen)(dppe)][PF$_6$] layered with Et_2O. The structure of the

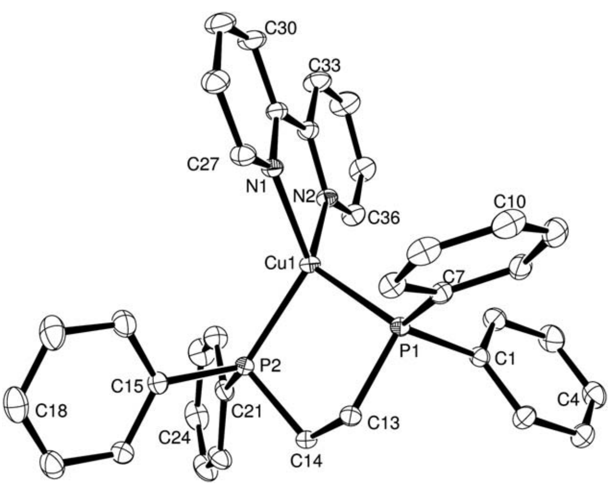


Fig. 2 Structure of the [Cu(bpy)(dppe)]$^+$ cation in 2{[Cu(bpy)(dppe)][PF$_6$]}·Et$_2$O·1.5CH$_2$Cl$_2$ with ellipsoids plotted at 30% probability level; H atoms are omitted. Selected bond parameters: Cu1–N1 = 2.0320(13), Cu1–N2 = 2.0337(15), Cu1–P2 = 2.2451(10), Cu1–P1 = 2.2496(11), P1–C1 = 1.8177(15), P1–C7 = 1.8189(16), P1–C13 = 1.8397(17), P2–C21 = 1.8214(17), P2–C15 = 1.8265(16), P2–C14 = 1.8388(17) Å; N1–Cu1–N2 = 80.91(6), N1–Cu1–P2 = 125.16(4), N2–Cu1–P2 = 121.72(5), N1–Cu1–P1 = 116.40(4), N2–Cu1–P1 = 125.27(5), P2–Cu1–P1 = 91.33(3)°.

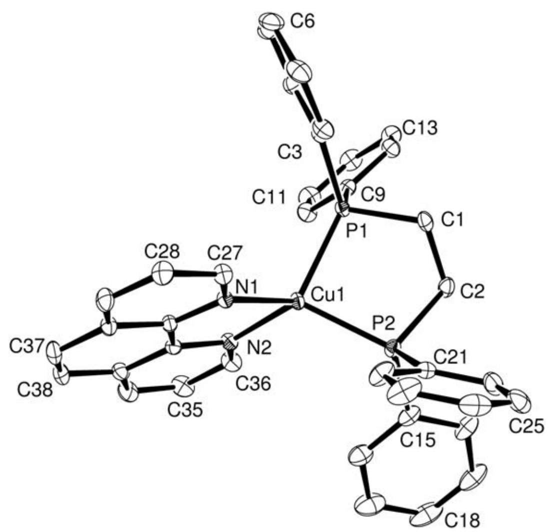


Fig. 4 Structure of the [Cu(phen)(dppe)]$^+$ cation in 2{[Cu(phen)(dppe)][PF$_6$]}·Et$_2$O·CH$_2$Cl$_2$ with ellipsoids plotted at 30% probability level; H atoms are omitted. Selected bond parameters: Cu1–N2 = 2.041(3), Cu1–N1 = 2.042(2), Cu1–P2 = 2.2390(9), Cu1–P1 = 2.2453(9), P1–C9 = 1.816(3), P1–C3 = 1.824(3), P1–C1 = 1.839(3), P2–C15 = 1.822(3), P2–C21 = 1.827(3), P2–C2 = 1.836(3) Å; N2–Cu1–N1 = 82.45(10), N2–Cu1–P2 = 120.45(8), N1–Cu1–P2 = 125.60(8), N2–Cu1–P1 = 124.69(8), N1–Cu1–P1 = 115.95(8), P2–Cu1–P1 = 91.57(3)°.

$[Cu(phen)(dppe)]^+$ cation and bond parameter data are given in Fig. 4. The angle between the N1Cu1N2 and P1Cu1P2 planes is 83.67(10)°. The structural determination revealed that the cations, anions and solvent molecules in $2\{[Cu(phen)(dppe)][PF_6]\}\cdot Et_2O\cdot CH_2Cl_2$ pack in an almost identical manner to those in $2\{[Cu(bpy)(dppe)][PF_6]\}\cdot Et_2O\cdot 1.5CH_2Cl_2$, despite the presence of the addition C_2-unit in the phen *versus* bpy ligand. Separation between the stacked pairs of phen units is 3.48 Å and between pairs of π-stacked phenyl rings is 3.77 Å. Pairwise stacking of phen ligands has also been observed in $[Cu(phen)(\mathbf{1})][BF_4]\cdot 1.5Et_2O\cdot MeCN$ but is not favoured once substituents are introduced in the 2- and 9-positions.[8] The addition of the two-carbon unit on going from $2\{[Cu(bpy)(dppe)][PF_6]\}\cdot Et_2O\cdot 1.5CH_2Cl_2$ to $2\{[Cu(phen)(dppe)][PF_6]\}\cdot Et_2O\cdot CH_2Cl_2$ results in a greater separation of the cations in the phen derivative and a lengthening of the *c*-axis. Along the chains shown in Fig. 3, the $Cu1\cdots Cu1^{iii}$ and $Cu1\cdots Cu1^{i}$ distances are 7.336(3) and 10.122(2) Å (symmetry codes *iii* and $i = 1 - x, -y, -z$ and $1 - x, -y, 1 - z$). On going to the phen derivative, the corresponding distances are 8.2624(14) and 10.0809(14) Å. The expansion from 7.336(3) to 8.2624(14) Å corresponds to the widening of the Cu···Cu separation across the bpy···bpy (Fig. 3) *versus* phen···phen inter-cation pairing.

Complexes with *P*,*S*-chelates

Although ligands **2** and **3** (Scheme 1) have been known for many years,[14,25,26] copper(I) complexes of these ligands have received little or no attention. A homoleptic copper(I) complex containing the ligand $Ph_2PCH_2CH_2SMe$ has been reported and structurally characterized.[27] The reaction of compound **2** with $[Cu(NCMe)_4][PF_6]$ in CH_2Cl_2 at room temperature for 2 hours, followed by addition of an equivalent of bpy resulted, not in the formation of $[Cu(\mathbf{2})(bpy)]^+$, but in the oxidative coupling of the thiol (Scheme 2) to give **5** which subsequently oxidizes to the bis(phosphine oxide) **6**.

It has previously been observed that the electrochemical oxidation of **2** proceeds with oxidation at phosphorus in addition to oxidative coupling to give a disulfide, and compound, **6**, has been crystallographically characterized.[28] In our hands, crystals of **6** grown from a CH_2Cl_2 solution overlaid with Et_2O proved to be a new polymorph. Both polymorphs crystallize in the *C*2/*c* space group but with cell dimensions of $a = 16.763(3)$, $b = 5.9420(12)$, $c = 30.238(6)$ Å, $\beta = 93.51(3)°$ (this work, **6**) and $a = 13.249(3)$, $b = 10.801(2)$, $c = 21.193(5)$ Å, $\beta = 104.50°$ (this form is denoted here as **6a**).[28] The molecular structure of the new polymorph of **6** is shown in Fig. 5 and selected bond parameters are listed in the caption. In both polymorphs, a 2-fold axis passes through the S–S bond. The torsion angle $C1–S1–S1^i–C1^i$ of 75.51(7)° in **6** compares with 81.34(15)° in **6a**. The presence of the 2-fold axis necessarily means that the two PO units in the molecule point out from the same side of the S–S bond, but Fig. 6 illustrates the significant difference in their orientations, and of that of the phenyl rings. In **6**, pairs of phenyl rings containing atoms C13 and $C13^{ii}$ (symmetry code $ii = -x, 1 - y, -z$) engage in face-to-face interactions at a separation of 3.25 Å, although this is in a less than optimal slipped arrangement. Repeated π-stacked motifs result in the assembly of chains of molecules running along the *c*-axis. Although the molecular packing in **6a** has not been discussed,[28] inspection of the structure (refcode COQJIB in the CSD[22]) reveals that similar face-to-face assemblies are not the predominant packing motifs. In both polymorphs, weak CH···O non-classical hydrogen bonds play a significant role in the packing.

Replacement of the SH by an SMe group produced a less easily oxidized *P*,*S*-ligand, **3**. The complex $[Cu(\mathbf{3})_2][PF_6]$ was isolated in good yield by the room temperature reaction of $[Cu(NCMe)_4][PF_6]$ with two equivalents of **3**. The highest mass peak in the electrospray ionization (ESI) mass spectrum appeared as *m*/*z* 678.9 and was assigned to $[M - PF_6]^+$. The ^{31}P NMR spectrum exhibited a singlet at δ −0.45 ppm and a septet at δ −143.2 ppm assigned to ligand and the $[PF_6]^-$ ion, respectively. The number of signals in the ^1H and ^{13}C NMR spectra were consistent with one ligand environment, and the observation of signals for the methyl group confirmed the retention of the MeS unit. The NMR

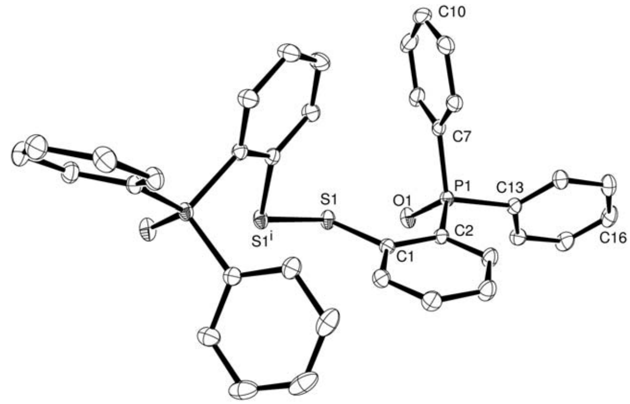
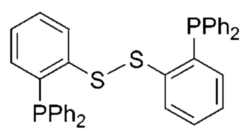


Fig. 5 Structure of compound **6** with ellipsoids plotted at 30% probability level (H atoms omitted). Symmetry code $i = -x, y, ½ - z$. Selected bond parameters: $S1–S1^i = 2.0375(7)$, $S1–C1 = 1.7915(14)$, $P1–O1 = 1.4868(11)$, $P1–C7 = 1.7986(14)$, $P1–C2 = 1.8042(13)$, $P1–C13 = 1.8052(13)$ Å; $C1–S1–S1^i = 104.80(5)$, $O1–P1–C7 = 112.94(6)$, $O1–P1–C2 = 112.08(6)$, $O1–P1–C13 = 110.62(6)°$.

$$2RSH \rightleftharpoons RSSR + 2H^+ + 2e^-$$



5

Scheme 2 Oxidative coupling of thiol to disulfide, in this case the conversion of **2** (Scheme 1) to **5**.

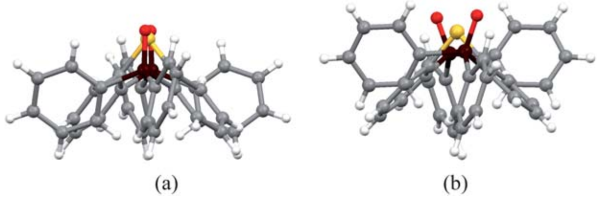


Fig. 6 Polymorphs (a) **6** and (b) **6a** viewed down the S–S bond. The PO units are shown in black.

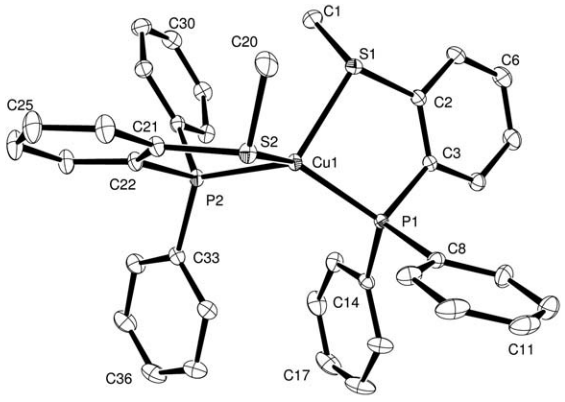


Fig. 7 Structure of the $[Cu(\mathbf{3})_2]^+$ cation in $[Cu(\mathbf{3})_2][PF_6]$ with ellipsoids plotted at 30% probability level and H atoms omitted. Selected bond parameters: Cu1–P1 = 2.2203(4), Cu1–P2 = 2.2258(5), Cu1–S1 = 2.3161(7), Cu1–S2 = 2.3163(4), S1–C2 = 1.7836(12), S1–C1 = 1.8077(13), P1–C8 = 1.8143(11), P1–C14 = 1.8146(11), P1–C3 = 1.8218(11), P2–C27 = 1.8119(12), P2–C33 = 1.8123(12), P2–C22 = 1.8210(11) Å; P1–Cu1–P2 = 123.391(16), P1–Cu1–S1 = 90.231(19), P2–Cu1–S1 = 122.229(19), P1–Cu1–S2 = 125.606(15), P2–Cu1–S2 = 90.922(17), S1–Cu1–S2 = 106.312(18)°.

spectra were assigned by routine 2D methods. The signal for C^{A1} (see Scheme 1) was readily assigned from an HMBC cross-peak to the methyl ^{1}H resonance at δ 2.27 ppm, and the signals for H^{A5} could then be assigned from the HMBC crosspeak to C^{A1}.

X-Ray quality crystals of $[Cu(\mathbf{3})_2][PF_6]$ were grown by diffusion of Et_2O into an MeCN solution of the complex. The structure of the cation is shown in Fig. 7. The Cu–S bonds are notably shorter than in $[Cu(Ph_2PCH_2CH_2SMe)_2][BF_4]$ (Cu–P = 2.2488(15) Å and Cu–S = 2.4088(18) Å, the Cu atom being on a 2-fold axis).[27] The angle between the P1CuS1 and P2Cu1S2 planes is 81.03(2)°. The degree of tilting from an idealized tetrahedral arrangement is assessed from the angles P2–Cu1–X, S2–Cu1–X, P1–Cu1–Y, S1–Cu1–Y where X and Y are the midpoints of the C2–C3 and C21–C22 bonds; these angles are, respectively, 131.0, 136.4, 149.7 and 119.7°. The tendency for the phenyl rings containing atoms C14 and C33 to participate in an intramolecular face-to-face interaction may contribute to the distortion, although the interaction is not at all ideal, with the angle between the least squares planes of the rings being 17.2°. The methyl group containing C1 lies over the π-system of the phenyl ring with C27 providing an additional intramolecular contact (C1···centroid = 3.6317(16) Å).[29] The $[PF_6]^-$ ion is disordered and has been modelled with a common P atom and two sets of F atoms with partial occupancies of 0.785 and 0.215. Pairs of cations (related by an inversion centre) in the unit cell interact efficiently with one another through a six-fold embrace between the phenyl rings of the ligands incorporating atoms P2 and S2 (Fig. 8). This embrace is reminiscent of those described in detail by Dance and Scudder.[30] Overall, the copper(I) centre is very efficiently protected in the crystalline state.

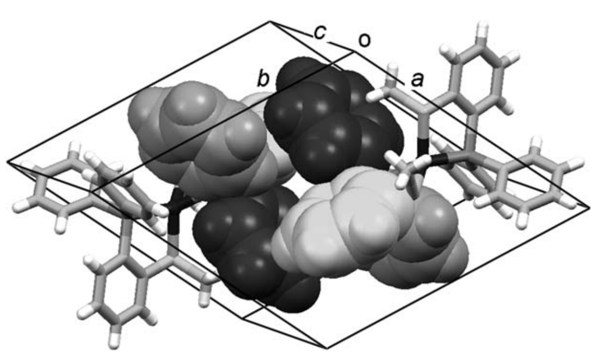


Fig. 8 Six-fold embrace of phenyl rings in between pairs of cations in the unit cell of $[Cu(\mathbf{3})_2][PF_6]$.

The heteroleptic complex $[Cu(\mathbf{1})(\mathbf{3})][PF_6]$ was prepared in 85.0% yield by treatment of $[Cu(NCMe)_4][PF_6]$ with ligand **1** followed by **3**. The ESI mass spectrum exhibited peaks at *m*/*z* 908.7 and 601.2, assigned to $[M - PF_6]^+$ and $[M - PF_6 - \mathbf{3}]^+$ respectively. The observed isotope distributions matched with those calculated. The ^{31}P NMR spectrum was consistent with the presence of the two ligands, a triplet at δ −2.1 ppm (J_{PP} = 64 Hz) and a doublet at δ −8.8 ppm (J_{PP} = 63 Hz) assigned to ligands **3** and **1**, respectively; the presence of the $[PF_6]^-$ counterion was confirmed by the observation of a characteristic septet at δ −143.2 ppm. The room temperature ^{1}H and ^{13}C NMR spectra were assigned by a combination of 2D techniques. Signals for protons H^{C5}, H^{A3} and H^{B4} overlapped (Fig. 9, 295 K spectrum) and the relative integral of this group of signals suggested the presence of a further resonance, tentatively assigned to H^{D4}; this was later confirmed from a variable temperature experiment (see below). Two extremely broad ^{1}H NMR resonances were observed at 295 K, centred at δ 7.3 and 6.7 ppm, and these were assigned to the *ortho* and *meta*-protons on the unsubstituted phenyl rings of ligand **1** (ring D). ^{1}H NMR spectra of the sample (in DMSO-d_6) were recorded up to 360 K (Fig. 9). On warming, the very broad signals disappeared, being replaced by a sharp triplet at δ 7.26 ppm assigned to H^{D3}, and a broadened multiplet at δ 7.04 ppm (H^{D2}). The assignments were confirmed by a COSY spectrum at 360 K, which also confirmed a value of δ 7.45 ppm for H^{D4}. It is clear from Fig. 9 that the signal at δ 7.04 ppm for H^{D2} at 360 K arises from an exchange process involving both the broad signals observed at 295 K. The large chemical shift difference between the two *ortho*-protons is consistent with the significantly different environments of these protons in the solid state (see below), one pointing towards the ether bridge of ligand **1** and one pointing away from it. The hindered rotation of phenyl

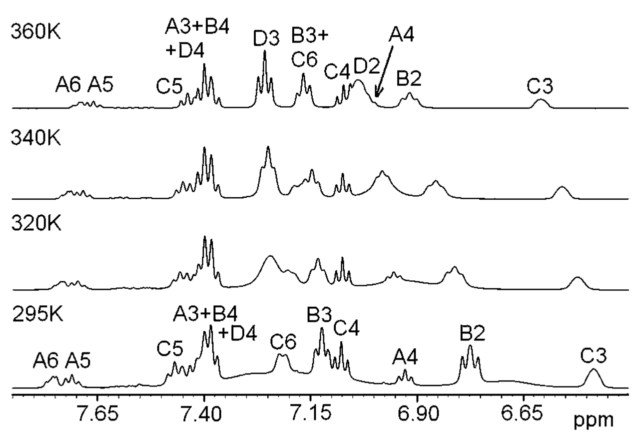


Fig. 9 Variable temperature 500 MHz ^{1}H NMR spectra of $[Cu(\mathbf{1})(\mathbf{3})][PF_6]$ in DMSO-d_6.

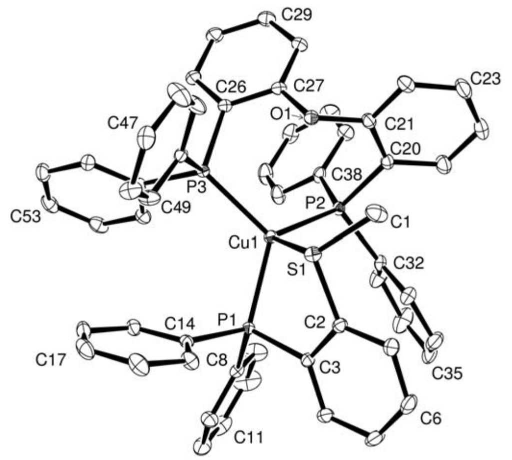


Fig. 10 Structure of the $[Cu(\mathbf{1})(\mathbf{3})]^+$ cation in $[Cu(\mathbf{1})(\mathbf{3})][PF_6]$ with ellipsoids plotted at 20% probability level (for clarity) and H atoms omitted. Selected bond distances and angles: Cu1–P1 = 2.2667(10), Cu1–P2 = 2.2681(10), Cu1–P3 = 2.2782(10), Cu1–S1 = 2.4614(11), S1–C1 = 1.796(4), S1–C2 = 1.772(4), O1–C21 = 1.400(4), O1–C27 = 1.391(4) Å; P1–Cu1–P2 = 122.33(4), P1–Cu1–P3 = 119.14(4), P2–Cu1–P3 = 112.96(4), P1–Cu1–S1 = 81.12(4), P2–Cu1–S1 = 107.16(4), P3–Cu1–S1 = 106.01(4), C2–S1–C1 = 103.8(2), C2–S1–Cu1 = 99.94(12), C1–S1–Cu1 = 122.39(15)°.

rings D is also consistent with the steric crowding of the ligands in the cation in the solid state structure described below.

Single crystals of $[Cu(\mathbf{1})(\mathbf{3})][PF_6]$ were grown within a few days by diffusion of Et_2O into a MeCN solution of the complex, and Fig. 10 depicts the structure of the $[Cu(\mathbf{1})(\mathbf{3})]^+$ cation. The Cu–S1 and Cu–P1 distances (ligand **3**) of 2.4614(11) and 2.2667(10) Å are significantly longer than those in $[Cu(\mathbf{3})_2][PF_6]$ (see caption to Fig. 7). As noted by other authors,[4,5,8] atom O1 of ligand **1** is at a non-bonded distance (3.067(2) Å) from the copper(I) centre. Consistent with the bulky nature of ligand **1** compared to **3**, the chelate angle of the former (P2–Cu1–P3 = 112.96(4)°) is significantly larger than that of the latter (P1–Cu1–S1 = 81.12(4)°). The P2Cu1P3 and P1Cu1S1 planes are orthogonal (the angle between the planes is 89.76(5)°), but the P2Cu1P3 unit is tilted towards atom S1 so that the angles S1–Cu1–X and P1–Cu1–X where X is the midpoint of the P2···P3 vector are 121.1 and 157.7°, respectively. (The position of the dummy atom was calculated using atom coordinates.) This distortion may well be driven, in part at least, by a CH···π interaction involving the methyl group (see below). The cation is sterically crowded. Each of the three PAr_3 units adopts the usual paddle-wheel arrangement. The arene rings engage in additional interactions: (i) there is an edge-to-face contact involving C49H49A and the phenyl ring containing atom C14 (H49A···centroid = 2.6 Å); (ii) the rings containing atoms C26 and C38 form a loose face-to-face interaction, but the angle between the least squares planes of the rings (26.2(2)°) prevent this from being very efficient; (iii) the methyl group lies over the π-cloud of the ring containing atom C20 (C1···centroid = 3.607(5) Å).[29] The net result is that the copper atom is well embedded within the ligand shell.

As analogs to $[Cu(bpy)(dppe)]^+$ and $[Cu(phen)(dppe)]^+$, we have also prepared $[Cu(bpy)(\mathbf{3})]^+$ and $[Cu(phen)(\mathbf{3})]^+$, both isolated as their hexafluoridophosphate salts from reactions of $[Cu(NCMe)_4][PF_6]$ with ligand **3** followed by either bpy or phen. Purification of $[Cu(bpy)(\mathbf{3})][PF_6]$ proved problematical, and even after several recrystallization attempts, a pure bulk sample could not be isolated. Recrystallization from CH_2Cl_2 layered with Et_2O resulted in the growth of a few X-ray quality yellow crystals of $[Cu(bpy)(\mathbf{3})][PF_6]$ and a small number of red crystals assumed to be $[Cu(bpy)_2][PF_6]$. The yields of the crystalline products were too low to allow spectroscopic characterization. However, an X-ray diffraction study (see below) confirmed the identity of $[Cu(bpy)(\mathbf{3})][PF_6]$. Purified $[Cu(phen)(\mathbf{3})][PF_6]$ was isolated in 88% yield, and the ESI mass spectrum exhibited a peak envelope at *m/z* 550.9 consistent with the $[M - PF_6]^+$ ion. Signals in the CD_3CN solution ^{31}P NMR spectrum at δ −2.1 and −143.1 ppm with approximately equal integrals, indicated the presence of ligand **3** and a $[PF_6]^-$ ion in a 1 : 1 ratio. The ^1H and ^{13}C NMR spectra were consistent with the presence of both phen and ligand **3** and were assigned by 2D techniques. Single crystals of $[Cu(phen)(\mathbf{3})][PF_6]\cdot CH_2Cl_2$ were grown by layering hexanes over a CH_2Cl_2 solution of the complex.

The structural parameters of the $[Cu(bpy)(\mathbf{3})]^+$ (Fig. 11) and $[Cu(phen)(\mathbf{3})]^+$ (Fig. 12) cations in $[Cu(bpy)(\mathbf{3})][PF_6]$ and $[Cu(phen)(\mathbf{3})][PF_6]\cdot CH_2Cl_2$ are similar. In $[Cu(bpy)(\mathbf{3})]^+$, the angle between the NCu1N2 and P1Cu1S1 planes is 87.67(7)°, and the corresponding angle in the phen derivative is 87.93(8)°. In each case, the diimine ligand is tilted towards the sulfur atom of ligand **3**. Defining X (the position being calculated using experimental atom coordinates) as the midpoint of the C24–C25 bond in each complex, the S1–Cu1–X and P1–Cu1–X angles are 113.7 and 156.5° in $[Cu(bpy)(\mathbf{3})]^+$, and 114.2 and 155.1° in $[Cu(phen)(\mathbf{3})]^+$. Although these distortions tend to bring the methyl group towards the π-cloud of a pyridine ring of bpy or phen, the $C_{Me}\cdots$centroid distances of 4.2 and 4.3 Å are too long to be consistent with a meaningful interaction. The packing of the cations in $[Cu(bpy)(\mathbf{3})][PF_6]$ differs significantly from that in $[Cu(phen)(\mathbf{3})][PF_6]\cdot CH_2Cl_2$. In the latter, the phen units form infinite π-stacked assemblies (Fig. 13a) with the distances between pairs of phen units being, alternately, 3.39 and 3.46 Å. The gap in the coordination sphere of Cu1 created by the tilting of the phen ligand is occupied by two carbon atoms of the phen

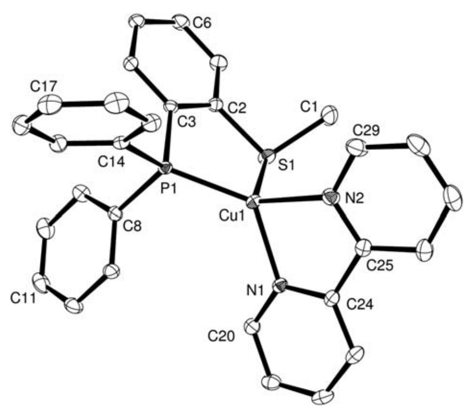


Fig. 11 Structure of the $[Cu(bpy)(\mathbf{3})]^+$ cation in $[Cu(bpy)(\mathbf{3})][PF_6]$ with ellipsoids plotted at 30% probability level; H atoms are omitted. Selected bond distances and angles: Cu1–N1 = 2.0359(16), Cu1–N2 = 2.0407(17), Cu1–P1 = 2.1824(6), Cu1–S1 = 2.3616(6), S1–C2 = 1.7842(19), S1–C1 = 1.812(3) Å; N1–Cu1–N2 = 81.09(7), N1–Cu1–P1 = 128.53(5), N2–Cu1–P1 = 138.98(5), N1–Cu1–S1 = 108.80(5), N2–Cu1–S1 = 109.02(5), P1–Cu1–S1 = 89.09(2)°.

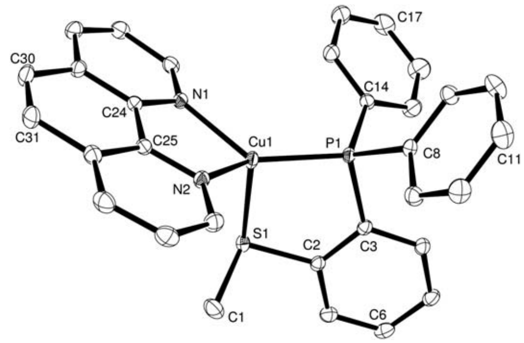


Fig. 12 Structure of the [Cu(phen)(**3**)]$^+$ cation in [Cu(phen)(**3**)][PF_6] with ellipsoids plotted at 30% probability level; H atoms are omitted. Selected bond distances and angles: Cu1–N2 = 2.0326(19), Cu1–N1 = 2.0487(18), Cu1–P1 = 2.1768(8), Cu1–S1 = 2.3412(7), S1–C2 = 1.774(2), S1–C1 = 1.811(3) Å; N2–Cu1–N1 = 82.47(7), N2–Cu1–P1 = 131.37(6), N1–Cu1–P1 = 133.24(5), N2–Cu1–S1 = 107.15(6), N1–Cu1–S1 = 111.10(6), P1–Cu1–S1 = 90.59(3)°.

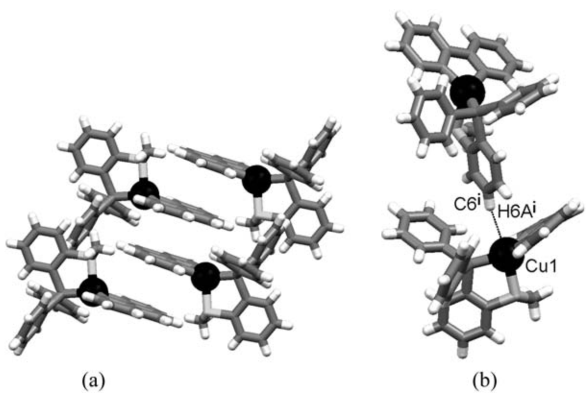


Fig. 13 (a) π-Stacking of phen units between cations in [Cu(phen)(**3**)][PF_6] and (b) close Cu···HC contacts between cations in [Cu(bpy)(**3**)].

ligand of the adjacent cation. Although this suggests a similar η^2-interaction as described in a number of systems,[31] the Cu1···C30^i (symmetry code $i = 2 - x, 2 - y, 1 - z$) separations of 3.92 and 3.72 Å indicate only a very weak interaction. More important is an edge-to-face interaction between phen C30H30A and the phenyl ring containing atom C8^i (H30A···centroid = 2.8 Å). No interaction face-to-face contacts are observed between bpy ligands in [Cu(bpy)(**3**)][PF_6]. The cations are packed so that the C6H6A unit of one phenyl ring is directed at the copper atom of an adjacent cation (Cu1···H6A^i = 2.9 Å, symmetry code $i = ½ + x, ½ - y, ½ + z$), and this fills the void in the coordination sphere of Cu1 (Fig. 13b). The phenyl ring containing atom C14 lies over the bpy ring containing N1^{ii} (symmetry code $i = ½ - x, ½ + y, ½ - z$), but an efficient face-to-face interaction[32] is prevented because the angle between the planes of the rings is 15.5°. The [PF_6]$^-$ ions are ordered and engage in extensive CH···F interactions. In both [Cu(bpy)(**3**)][PF_6] and [Cu(phen)(**3**)][PF_6]·CH_2Cl_2, the geometries of the coordination spheres in the cations show significant deviation from ideal tetrahedral arrangements.

Phenyl–bpy stacking interactions in [Cu(4)$_2$][PF_6]

The complexes described so far contain either one or two soft, bidentate donor sets. We were also intrigued to find out whether the presence of phenyl substituents in the 6-position of bpy would lead to a less flexible copper-coordination shell by introducing intra-cation phenyl–bpy stacking interactions. We have recently reported this phenomenon in [Ir(ppy)$_2$(Hpbpy)][PF_6] and related complexes (Hppy = 2-phenylpyridine, Hpbpy = 6-phenyl-2,2′-bipyridine) and the remarkable effect that it has on the lifetimes of LEECs employing these complexes.[33–37] Although the crystal structure of [CuL_2][BF_4] where L = 4,4′-dimethyl-6,6′-diphenyl-2,2′-bipyridine has been reported, the role of phenyl–bpy π-stacking was not described; this complex is weakly emissive ($\Phi_{em} = 2.7 \times 10^{-4}$ in CH_2Cl_2 solution).[38]

The complex [Cu(**4**)$_2$][PF_6] was isolated in near quantitative yield after reaction of [Cu(NCMe)$_4$][PF_6] with ligand **4** (Scheme 1) followed by work up. In the ESI mass spectrum, the highest mass peak envelope at *m*/*z* 554.9 was assigned to [M − PF_6]$^+$. The solution ^{1}H and ^{13}C NMR spectra were consistent with one ligand environment. The spectra were fully assigned using 2D techniques, starting first with an HMBC cross-peak between the ^{13}C NMR signal for the methyl group and the ^{1}H NMR resonance for H^{A5} which allowed the latter to be assigned.

Single crystals of [Cu(**4**)$_2$][PF_6] suitable for X-ray diffraction were grown from an MeCN solution of the complex into which Et_2O vapour was allowed to diffuse over several days. Fig. 14 depicts the structure of the [Cu(**4**)$_2$]$^+$ cation, and bond distances and angles within the coordination shell are given in the caption. Atom Cu1 is in a distorted tetrahedral environment, the angle between the N1Cu1N2 and N3Cu1N4 planes being 76.09(9)°. The two ligands are tilted with respect to one another such that the angles N3–Cu1–X and N4–Cu1–X (X = midpoint of C6–C7) are 155.2 and 121.4°, and angles N1–Cu1–X′ and N2–Cu1–X′ (X′ = midpoint of C23–C24) are 155.7 and 120.8°, respectively. This distortion facilitates face-to-face interactions between the phenyl and pyridine rings containing C29 and N2 (separation = 3.7 Å) and between phenyl and pyridine rings containing C12 and N4 (separation = 3.4 Å). Each π-stack involves a phenyl-substituted pyridine ring, and both are in optimized offset arrangements (Fig. 15).

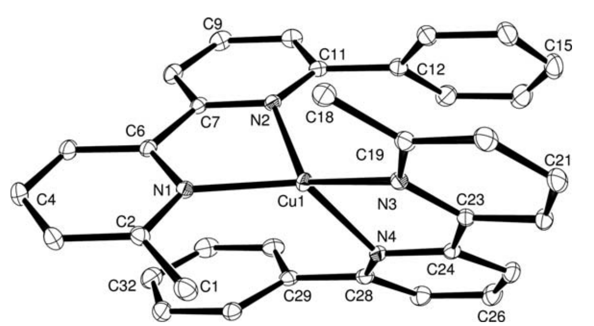


Fig. 14 Structure of the [Cu(**4**)$_2$]$^+$ cation in [Cu(**4**)$_2$][PF_6] with ellipsoids plotted at 30% probability level; H atoms are omitted. Selected bond parameters: Cu1–N3 = 2.0018(14), Cu1–N1 = 2.0038(14), Cu1–N2 = 2.0580(14), Cu1–N4 = 2.0712(14) Å; N3–Cu1–N1 = 133.57(6), N3–Cu1–N2 = 129.48(6), N1–Cu1–N2 = 81.41(6), N3–Cu1–N4 = 81.17(6), N1–Cu1–N4 = 129.45(6), N2–Cu1–N4 = 104.20(6)°.

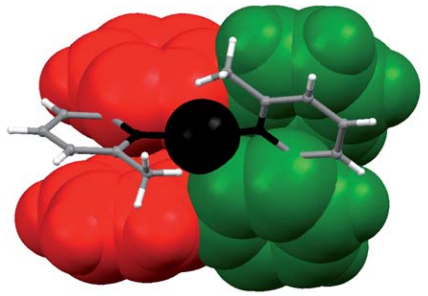


Fig. 15 Intra-cation phenyl–pyridine π-stacking in $[Cu(\mathbf{4})_2]^+$ (see text for details). Ball-and-stick representation is used for the methylpyridine rings not involved in these interactions.

Distortion analysis using the White model

In the structural discussions above, we have described the distortion away from a tetrahedral coordination sphere in terms of the tilting of one ligand along a pathway that could ultimately lead to a square planar arrangement. Of the seven complexes studied, this analysis reveals that there is significant distortion in complexes involving *P*,*S*-chelate **3** attributed to $CH_{methyl}\cdots\pi$ contacts, and in $[Cu(\mathbf{4})_2][PF_6]$ arising from π-stacking interactions. A more rigorous analysis can be carried out using the model introduced by White.[39] The model was developed for a series of copper(I) bis(phen) and bis(bpy) complexes, and defines angles θ_x, θ_y and θ_z which, for ideal D_{2d} symmetry, would all be 90°. The deviation of angle θ_z away from 90° indicates a lowering of symmetry from D_{2d} to D_2, ultimately giving D_{2h} (square planar bis(chelate)). Angles θ_x and θ_y describe the degree of 'rocking' or 'wagging'[39] of the second ligand with respect to the first. In White's original analysis, it was concluded that ranges of $81.8° \leq \theta_x \leq 93.9°$, $83.2° \leq \theta_y \leq 92.6°$ and $98.2° \leq \theta_z \leq 107.6°$ were a consequence of crystal packing forces. In a separate study of a series of salts containing $[Cu(2,9\text{-}Me_2phen)_2]^+$ with different counterions, differences in crystal packing forces lead to values of $78.2° \leq \theta_x \leq 89.8°$, $74.0° \leq \theta_y \leq 86.0°$ and $72.8° \leq \theta_z \leq 88.1°$.[40] The cation in $[Cu(2\text{-}MeOC_6H_4phen)_2][PF_6]$ (2-$MeOC_6H_4$phen = 2-(4-methoxyphenyl)-1,10-phenanthroline) exhibits severe distortion in the solid state with θ_x, θ_y and θ_z being 77.6, 106.9 and 107.5°, respectively, which is attributed to intra-cation face-to-face π-stacking between a pendant aryl ring and phen domain.[41] Related intra-cation interactions occur in copper(I) complexes containing phen and diketimine ligands with pendant benzyl substituents.[42] Table 1 summarizes values of θ_x, θ_y and θ_z for the complexes structurally characterized in this work. The largest distortions are observed for $[Cu(\mathbf{4})_2][PF_6]$ and originate in intra-cation phenyl–bpy π-stacking. Complexes incorporating the *P*,*S*-chelate **3** are subject to significant deviations in θ_x or θ_y, but show little distortion along the tetrahedral-to-square planar pathway. The cations in $[Cu(bpy)(dppe)][PF_6]$ and $[Cu(phen)(dppe)][PF_6]$ exhibit the smallest distortions away from an ideal tetrahedral coordination sphere.

Table 1 Orientation angles (defined in ref. 39) for the copper(I) complexes in this work

Complex	$\theta_x/°$	$\theta_y/°$	$\theta_z/°$
$[Cu(\mathbf{4})_2][PF_6]$	100.3	102.9	76.7
$[Cu(bpy)(dppe)][PF_6]$	88.2	87.4	84.3
$[Cu(phen)(dppe)][PF_6]$	88.0	88.2	83.7
$[Cu(\mathbf{3})_2][PF_6]$	95.0	99.2	81.2
$[Cu(\mathbf{1})(\mathbf{3})][PF_6]$	91.7	108.3	90.2
$[Cu(bpy)(\mathbf{3})][PF_6]$	110.3	85.8	87.7
$[Cu(phen)(\mathbf{3})][PF_6]$	108.8	92.8	87.9

Absorption and emission properties

The electronic absorption spectra of CH_2Cl_2 solutions of the complexes were dominated by absorptions in the UV region arising from ligand-centred $\pi^* \leftarrow \pi$ transitions. Each of the coloured complexes exhibited a broad MLCT band in the visible region (408 nm for $[Cu(bpy)(dppe)][PF_6]$, 420 nm for $[Cu(phen)(dppe)][PF_6]$, 394 nm for $[Cu(phen)(\mathbf{3})][PF_6]$, 453 and 536 nm for $[Cu(\mathbf{4})_2][PF_6]$). Cationic copper(I) complexes show luminescence originating from the metal-to-ligand charge transfer states if ligand-centred π*-orbitals are easily accessible.[43] Preliminary screening of the emissive behaviour of the complexes confirmed that all but $[Cu(\mathbf{3})_2][PF_6]$ exhibited fluorescence when excited at a wavelength corresponding to the maximum in the electronic spectrum. However, we observed that the absorption spectra of the complexes lost intensity after the emission measurements, suggesting that partial decomposition of the samples was occurring. We are currently investigating the photophysical behaviour of these materials in thin films (PMMA or PS) in which decomposition through disproportionation or other mechanisms is expected to be reduced.

Conclusions

We have described preparation of a series of heteroleptic $[Cu(N,N)(P,P)]^+$ and $[Cu(N,N)(P,S)]^+$ complexes which capitalizes the fact that the heteroleptic species are favoured in solution over the respective homoleptic complexes. Structural characterization of all the complexes has allowed us to assess the degree of distortion of the coordination shell of the copper(I) ion away from ideal tetrahedral which is defined in the White model as having $\theta_x = \theta_y = \theta_z = 90°$. The greatest distortion along a pathway towards square planar coordination is observed in the homoleptic complex $[Cu(\mathbf{4})_2][PF_6]$ and arises from intra-cation π-stacking between phenyl and bpy domains. All the complexes which contain the *P*,*S*-chelating ligand **3** exhibit significant deviations in θ_x or θ_y ('rocking' or 'waggling' distortions) which are associated with intra-cation $CH_{methyl}\cdots\pi$ contacts. Their extent can also be assessed through a less rigorous, but nonetheless informative, approach by measuring the S–Cu–X and P–Cu–X angles where the S and P atoms reside in *P*,*S*-chelate **3** and X is the midpoint of the backbone of the second ligand. Despite suffering these distortions, the *P*,*S*-chelate containing complexes $[Cu(\mathbf{3})_2][PF_6]$ and $[Cu(\mathbf{1})(\mathbf{3})][PF_6]$ in particular exhibit embraces between the phenyl substituents that lead to the copper(I) centre being sterically protected. In $[Cu(\mathbf{1})(\mathbf{3})][PF_6]$, this leads to hindered rotation of phenyl rings in solution. We expect that in these two complexes in particular, geometric relaxation of the excited state should be minimized.

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