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Metal complexes of sterically hindered pyrazolylpyridines. The single crystal X-ray structure of $[Cu(L^1)_2]BF_4$ (L^1 = 1-{pyrid-2-yl}-3-{2′,5′-dimethoxyphenyl}pyrazole)

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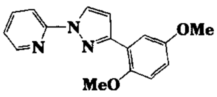
Abstract—Reaction of potassium 3{5}-(3′,4′-dimethoxyphenyl)pyrazolide with 2-bromopyridine in diglyme at 130°C for 3 days followed by an aqueous quench, affords 1-{pyrid-2-yl}-3-{3′,4′-dimethoxyphenyl}pyrazole (L^2) in 69% yield after recrystallisation from hot hexanes. Complexation of $[Cu(NCMe)_4]BF_4$ by 2 molar equivalents of 1-{pyrid-2-yl}-3-{2′,5′-dimethoxyphenyl}pyrazole (L^1) or L^2 in MeCN at room temperature, followed by concentration and crystallisation with Et_2O, gives $[Cu(L)_2]BF_4$ ($L = L^1$, L^2) in good yields. Treatment of $AgBF_4$ with L^1 or L^2 in $MeNO_2$ similarly gives $[Ag(L)_2]BF_4$ ($L = L^1$, L^2); reaction of $AgBF_4$ with L^2 in MeCN gives a product of stoichiometry $[Ag(L^2)(NCMe)]BF_4$. The ^1H NMR spectra of the $[M(L)_2]BF_4$ complexes show peaks arising from a single coordinated ligand environment. The single crystal X-ray structure of $[Cu(L^1)_2]BF_4$ shows a tetrahedral complex cation with Cu—N = 2.011(8), 2.036(8), 2.039(8), 2.110(8) Å. The Cu^I centre is close to tetrahedral, the dihedral angle between the least-squares planes formed by the Cu atom and the N donor atoms of the two ligands being 88.3(3)°. Complexation of hydrated $Cu(BF_4)_2$ by L^2 in MeCN at room temperature yields $[Cu(L^2)_2](BF_4)_2$. The cyclic voltammograms of the three Ag^I complexes in MeCN/0.1 M Bu^n_4 NPF_6 are suggestive of extensive ligand dissociation in this solvent. © 1997 Elsevier Science Ltd

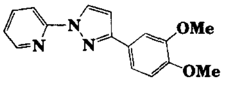
Keywords: copper; silver; pyrazolylpyridine; crystal structure.

INTRODUCTION

We have recently reported a structural and electrochemical study of a series of complexes of formula $[Cu(L^1)(Tp^R)]BF_4$ (L^1 = 1-{pyrid-2-yl}-3-{2′,5′-dimethoxyphenyl}pyrazole; $[Tp^R]^-$ = *tris*-{3-arylpyrazolyl}borate), together with the homoleptic complex $[Cu(L^1)_2](BF_4)_2$ [1]. A single crystal X-ray structure of the latter compound showed the presence of unexpected 2.9 Å contacts between the Cu^{II} ion and 2′-methoxy oxygen atoms of the coordinated ligands, which appeared to be maintained in solution. We were therefore interested to compare its properties with those of its Cu^I congener. The syntheses and electrochemistry of $[M(L^1)_2]BF_4$ ($M^+ = Cu^+$, Ag^+) are reported here, together with a structure determination of the Cu^I compound. The preparation and Cu^I, Cu^{II} and Ag^I complex chemistry of the structurally isomeric ligand 1-{pyrid-2-yl}-3-{3′,4′-dimethoxyphenyl}pyrazole (L^2) are also described.



L^1



L^2

EXPERIMENTAL

Unless otherwise stated, all manipulations were carried out in air. 2-Bromopyridine (Avocado), KH (40% suspension in mineral oil), $Cu(BF_4)_2 \cdot xH_2O$ ($x \approx 4$), $AgBF_4$ (Aldrich) and all solvents were used as supplied, except that diglyme was dried over sodium before use. 3{5}-(3′,4′-Dimethoxyphenyl)pyrazole

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[2], L^1 [1], $[Cu(NCMe)_4]BF_4$ [3] and $[Cu(L^1)_2](BF_4)_2$ (**III**) [1] were prepared by the literature procedures.

Synthesis of 1-(*pyrid*-2-*yl*)-3-(3′,4′-*dimethoxyphenyl*) *pyrazole* (L_2)

A mixture of 3{5}-(3′,4′-dimethoxyphenyl) pyrazole (10.0 g, 0.049 mol) and KH (2.0 g, 0.049 mol) was stirred in diglyme (60 cm^3) at room temperature under N_2 for 1 h, giving a gelatinous white precipitate. 2-Bromopyridine (7.8 g, 0.049 mol) was then added, and the mixture stirred under N_2 at 130°C for 3 days. The solution was quenched with an equal volume of water, and refrigerated overnight. The resultant white solid was filtered, washed with hot saturated aqueous KOH (to remove any unreacted pyrazole) and with water, and dried over P_2O_5. Recrystallisation from hot hexanes yielded white microcrystals (yield 9.8 g, 71%). Found: C, 68.4; H, 5.3; N, 15.1. Calc. for $C_{16}H_{15}N_3O_2$: C, 68.3; H, 5.4; N, 14.9%. M.p. 117–119°C. IR (cm^{-1}): 1595m, 1507s, 1477m, 1453s, 1434m, 1356m, 1246m, 1145m, 1036m, 1022m, 952m, 873m, 764m, 720m. UV (CH_3CN): $\lambda_{max} = 211$ nm ($\varepsilon_{max} = 29{,}800\ M^{-1}\ cm^{-1}$), 246 (sh), 278 (sh), 288 (18,400), 307 (27,900), 318 (sh). EI mass spectrum (fragment, %): m/z 281 ($[M]^+$, 100), 266 ($[M\text{-}CH_3]^+$, 20), 238 ($[M\text{-}COCH_3]^+$, 24), 194 ($[M\text{-}(COCH_3)_2\text{-}H]^+$, 18), 78 ($[C_5H_4N]^+$, 58). NMR spectra ($CDCl_3$, 293 K): ^1H; δ 8.56 (d, 2.7 Hz, 1H, Pz H^5), 8.39 (br d, 4.8 Hz, 1H, Py H^6), 8.07 (d, 8.3 Hz, 1H, Py H^3), 7.79 (ddd, 8.3, 7.3 and 1.9 Hz, 1H, Py H^4), 7.51 (d, 1.9 Hz, 1H, Ph H^2), 7.40 (dd, 8.4 and 1.9 Hz, 1H, Ph H^5), 7.15 (dd, 7.3 and 4.9 Hz, 1H, Py H^5), 6.91 (d, 8.4 Hz, 1H, Ph H^6), 6.71 (d, 2.7 Hz, 1H, Pz H^4), 3.98 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3). ^{13}C; δ 153.6, 151.6, 149.4, 149.2 (Py C^2 + Pz C^3 + Ph C^2 + Ph C^5), 147.9 (Py C^6), 138.6 (Py C^4), 128.2 (Pz C^5), 126.0 (Ph C^1), 121.1, 118.7 (Py C^3 + PyC^5), 112.4, 111.2, 108.9 (Ph C^3 + Ph C^4 + Ph C^6), 105.0 (Pz C^4), 55.9 ($2 \times OCH_3$).

Synthesis of Bis-[1-(*pyrid*-2-*yl*)-3-(2′,5′-*dimethoxyphenyl*)*pyrazole*]*copper*(*I*) *tetrafluoroborate* (**I**)

L^1 (0.15 g, 5.34×10^{-4} mol) was added to a solution of $[Cu(NCMe)_4]BF_4$ (0.083 g, 2.67×10^{-4} mol) in MeCN (20 cm^3), and the mixture stirred under N_2 for 15 min. The resultant deep yellow solution was reduced under vacuum to 2 cm^3 volume, and layered with Et_2O to afford yellow plates (yield 0.17 g, 89%). Found: C, 53.8; H, 4.2; N, 11.9. Calc. for $C_{32}H_{30}N_6O_4BF_4Cu$: C, 53.9; H, 4.2; N, 11.8%. IR (cm^{-1}): 1607m, 1526s, 1489s, 14445, 1343m, 1330m, 1288m, 1260m, 1240m, 1218s, 1185m, 1060vs, 1049m, 1030m, 950m, 810m, 783m, 733m, 720m, 521m. UV (CH_3CN): $\lambda_{max} = 209$ nm ($\varepsilon_{max} = 74{,}500\ M^{-1}\ cm^{-1}$), 229 (sh), 260 (sh), 279 (sh), 294 (33,900), 320 (28,400). FAB mass spectrum (fragment, %): 625 ($[^{63}Cu(L^1)_2]^+$, 100), 344 ($[^{63}Cu(L^1)]^+$, 60), 329 ($[^{63}Cu(L^1\text{-}CH_3)]^+$, 38), 314 ($[^{63}Cu(L^1\text{-}2CH_3)]^+$, 29). ^1H NMR ($\{CD_3\}_2CO$, 233 K): δ 9.18 (br s, 1H, Py H^6), 8.64 (d, 2.7 Hz, 1H, Pz H^5), 8.41 (d, 8.2 Hz, 1H, Py H^3), 8.36 (dd, 8.2 and 7.2 Hz, 1H, Py H^4), 7.56 (dd, 7.2 and 4.2 Hz, 1H, Py H^5), 7.43 (d, 2.7 Hz, 1H, Pz H^4), 7.38 (d, 2.9 Hz, 1H, Ph H^6), 6.98 (d, 8.9 Hz, 1H, Ph H^3), 6.80 (dd, 8.9 and 2.9 Hz, 1H, Ph H^4), 3.82 (s, 3H, OCH_3), 3.17 (s, 3H, OCH_3).

Synthesis of Bis-[1-(*pyrid*-2-*yl*)-3-(3′,4′-*dimethoxyphenyl*)*pyrazole*]*copper*(*I*) *tetrafluoroborate* (**II**)

Method as for **I**, using L^2 (0.15 g, 5.34×10^{-4} mol). The product was obtained as yellow platelets from $MeCN/Et_2O$ (yield 0.16 g, 81%). Found: C, 53.2; H, 4.3; N, 11.3. Calc. for $C_{32}H_{30}N_6O_4BF_4Cu$: C, 53.9; H, 4.2; N, 11.8%. IR (cm^{-1}): 1605m, 1515s, 1456s, 1444s, 1360m, 1322m, 1263m, 1246m, 1231m, 1060vs, 1022m, 949m, 772m, 521m. UV (CH_3CN): $\lambda_{max} = 210$ nm ($\varepsilon_{max} = 70{,}800\ M^{-1}\ cm^{-1}$), 242 (sh), 278 (sh), 289 (sh), 307 (49,800), 321 (sh). FAB mass spectrum (fragment, %): 625 ($[^{63}Cu(L^2)_2]^+$, 88), 344 ($[^{63}Cu(L^2)]^+$, 100), 329 ($[^{63}Cu(L^2\text{-}CH_3)]^+$, 7). ^1H NMR ($\{CD_3\}_2CO$, 233 K): δ 9.14 (br d, 4.9 Hz, 1H, Py H^6), 8.54 (d, 2.9 Hz, 1H, Pz H^5), 8.34–8.26 (m, 2H, Py H^3 + Py H^4), 7.80 (br s, 1H, Ph H^2), 7.58 (dd, 7.7 and 4.9 Hz, 1H, Py H^5), 7.50 (dd, 8.5 and 2.3 Hz, 1H, Ph H^5), 7.47 (d, 2.9 Hz, 1H, Pz H^4), 6.89 (d, 8.5 Hz, 1H, Ph H^6), 3.69 (s, 3H, OCH_3), 3.08 (s, 3H, OCH_3).

Synthesis of Bis-[1-(*pyrid*-2-*yl*)-3-(3′,4′-*dimethoxyphenyl*)*pyrazole*]*copper*(*II*) *ditetrafluoroborate* (**IV**)

$Cu(BF_4)_2 \cdot xH_2O$ (0.083 g, 2.67×10^{-4} mol) and L^2 (0.15 g, 5.34×10^{-4} mol) were stirred in MeCN (10 cm^3) for 30 min, yielding a mauve solution which was filtered and reduced to 3 cm^3 in volume. Vapour diffusion of Et_2O into the resultant solution afforded feathery blue-violet needles (yield 0.16 g, 73%). Found: C 48.1; H, 3.9; N, 11.2. Calc. for $C_{32}H_{30}N_6O_4B_2F_8$ Cu: C, 48.1; H, 3.8; N, 10.5%. IR (cm^{-1}): 1616m, 1508s, 1468m, 1332m, 1258s, 1060vs, 978m, 951m, 784m, 766m, 521m. UV/vis (CH_3CN): $\lambda_{max} = 240$ nm ($\varepsilon_{max} = 41{,}600\ M^{-1}\ cm^{-1}$), 266 (sh), 290 (sh), 319 (46,300), 332 (sh), 504 (100), 695 (64), 885 (sh). UV/vis (CH_3NO_2): $\lambda_{max} = 683$ nm ($\varepsilon_{max} = 185\ M^{-1}\ cm^{-1}$). UV/vis ($\{CH_3\}_2CO$): $\lambda_{max} = 463$ nm (sh), 703 ($\varepsilon_{max} = 70\ M^{-1}\ cm^{-1}$), 890 (sh). FAB mass spectrum (fragment, %): 625 ($[^{63}Cu(L^2)_2)]^+$, 55), 344 ($[^{63}Cu(L^2)]^+$, 100), 329 ($[^{63}Cu(L^2\text{-}CH_3)]^+$, 9), 314 ($[^{63}Cu(L^2\text{-}2CH_3)]^+$, 9).

Synthesis of Bis-[1-(*pyrid*-2-*yl*)-3-(2′,5′-*dimethoxyphenyl*)*pyrazole*]*silver*(*I*) *tetrafluoroborate* (**V**)

A mixture of L^1 (0.15 g, 5.34×10^{-4} mol) and $AgBF_4$ (0.052 g, 2.67×10^{-4} mol) in $MeNO_2$ (10 cm^3) was stirred at room temperature for 15 min. The pale yellow solution was filtered, and reduced to 2 cm^3 volume. Vapour diffusion of Et_2O into the solution (which was kept in the dark) afforded colourless plates (yield 0.12 g, 59%). Found: C, 50.6; H, 4.0; N, 11.1. Calc. for $C_{32}N_{30}N_6O_4BF_4Ag$: C, 50.8; H, 4.0; N, 11.1%. IR (cm^{-1}): 1605m, 1530s, 1488s, 1442s, 1356m, 1326m, 1286m, 1242m, 1218s, 1183m, 1060vs, 952m, 804m, 778m, 734m, 521m. UV (CH_3CN): $\lambda_{max} = 208$ nm ($\varepsilon_{max} = 74{,}200$ M^{-1} cm^{-1}), 229 (sh), 261 (sh), 279 (sh), 294 (33,600), 319 (28,500). FAB mass spectrum (fragment, %): 669 ($[^{107}Ag(L^1)_2]^+$, 21), 388 ($[^{107}Ag(L^1)]^+$, 100), 373 ($[^{107}Ag(L^1\text{-}CH_3)]^+$, 15), 358 ($[^{107}Ag(L^1\text{-}2CH_3)]^+$, 32), 282 ($(L^1+H]^+$, 8), 281 ($[L^1]^+$, 10). ^1H NMR ($\{CD_3\}_2CO$, 293 K): δ 8.85 (d, 2.7 Hz, 1H, Pz H^5), 8.59 (br d, 5.0 Hz, 1H, Py H^6), 8.17–8.27 (m, 2H, Py H^3 + Py H^4), 7.51 (ddd, 6.8, 5.0 and 1.7 Hz, 1H, Py H^5), 7.48 (d, 3.1 Hz, 1H, Ph H^6), 7.18 (d, 2.8 Hz, 1H, Pz H^4), 6.98 (d, 9.0 Hz, 1H, Ph H^3), 6.83 (dd, 9.0 and 3.1 Hz, 1H, Ph H^4), 3.78 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3).

Synthesis of Bis-[1-(*pyrid-2-yl*)-3-(3′,4′-*dimethoxyphenyl*)*pyrazole*]*silver*(*I*) *tetrafluoroborate* (**VI**)

Method as for **V**, using L^2 (0.15 g, 5.34×10^{-4} mol). The product was isolated as feathery colourless needles from $MeNO_2Et_2O$ (yield 0.14 g, 69%). Found: C, 48.2; H, 3.9; N, 11.1. Calc. for $C_{32}H_{30}N_6O_4BF_4Ag \cdot CH_3NO_2$: C, 48.4; H, 4.1; N, 12.0%. IR (cm^{-1}): 1603m, 1514s, 1440s, 1395m, 1357m, 1323m, 1250s, 1226m, 1060vs, 952m, 854m, 778m, 718m, 640m, 521m. UV (CH_3CN): $\lambda_{max} = 208$ nm ($\varepsilon_{max} = 74{,}200$ M^{-1} cm^{-1}), 229 (sh), 261 (sh), 279 (sh), 294 (33,600), 319 (28,500). FAB mass spectrum (fragment, %): 669 ($[^{107}Ag(L^2)_2]^+$, 31), 388 ($[^{107}Ag(L^2)]^+$, 100), 373 ($[^{107}Ag(L^2\text{-}CH_3)]^+$, 7), 358 ($[^{107}Ag(L^2\text{-}2CH_3)]^+$, 8), 282 ($[L^1+H]^+$, 14), 281 ($[L^1]^+$, 24). ^1H NMR ($\{CD_3\}_2CO$, 293 K): δ 8.90 (d, 2.8 Hz, 1H, Pz H^5), 8.63 (br d, 4.8 Hz, 1H, Py H^6), 8.29 (ddd, 8.3, 7.0 and 1.7 Hz, 1H, Py H^4), 8.19 (d, 8.3 Hz, 1H, Py H^3), 7.48–7.58 (m, 2H, Py H^5 + Ph H^2), 7.48 (dd, 8.4 and 2.1 Hz, 1H, Ph H^5), 7.21 (d, 2.8 Hz, 1H, Pz H^4), 6.82 (d, 8.4 Hz, 1H, Ph H^6), 3.77 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3).

Synthesis of [1-(*pyrid-2-yl*)-3-(3′,4′-*dimethoxyphenyl*) *pyrazole*][*acetonitrile*]*silver*(*I*) *tetrafluoroborate* (**VII**)

A MeCN (10 cm^3) solution of L^2 (0.15 g, 5.34×10^{-4} mol) and $AgBF_4$ (0.104 g, 5.34×10^{-4} mol) was stirred at room temperature for 15 minutes. Following concentration to 2 cm^3 and filtration, the product was isolated as feathery colourless needles by vapour diffusion of Et_2O into the resultant solution (yield 0.22 g, 79%). Found: C, 41.6; H, 3.5; N, 10.5. Calc. for $C_{18}H_{18}N_4O_2BF_4Ag$: C, 41.8; H, 3.5; N, 10.8% IR (cm^{-1}): 2320w, 2284w, 1604m, 1514s, 1445s, 1326m, 1256m, 1060vs, 954m, 842m, 779s, 718m, 639m, 521m. UV(CH_3CN): $\lambda_{max} = 211$ nm ($\varepsilon_{max} = 28{,}200$ M^{-1} cm^{-1}), 246 (11,100), 278 (sh), 288 (17,800), 307 (26,900), 316 (sh). FAB mass spectrum (fragment, %): 669 ($[^{107}Ag(L^2)_2]^+$, 41), 388 ($[^{107}Ag(L^2)]^+$, 100), 358 ($[^{107}Ag(L^2\text{-}2CH_3)]^+$, 14), 282 ($[L^2+H]^+$, 22), 281 ($[L^2]^+$, 28). ^1H NMR (CD_3NO_2, 293 K): δ 8.45 (d, 2.8 Hz, 1H, Pz H^5), 8.44 (br d, 5.1 Hz, 1H, Py H^6), 8.13 (ddd, 8.5, 7.4 and 1.8 Hz, 1H, Py H^4), 7.81 (d, 8.5 Hz, 1H, Py H^3), 7.48 (ddd, 7.4, 5.1 and 0.8 Hz, 1H, Py H_5), 7.40–7.44 (m, 2H, Ph H^2 + Ph H^5), 7.01 (d, 2.8 Hz, 1H, Pz H^4), 6.89 (d, 8.5 Hz, 1H, Ph H^6), 3.80 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 2.24 (s, 3H, $NCCH_3$).

X-ray structure determination of $[Cu(L^1)_2]BF_4$ (**I**)

Vapour diffusion of Et_2O into a solution of the complex in MeCN yielded a small number of weakly diffracting crystals. Experimental details of the structure determination are given in Table 1. The structure was solved by direct methods (SHELXTL PLUS [4]) and refined by full matrix least-squares of F^2 (SHELXL 93 [5]). High temperature factors on one dimethoxyphenyl group (C(13)—C(22)) are suggestive of librational disorder involving this residue, which may be related to the relatively long contact between this group and its nearest neighbour in the crystal lattice (*vide infra*). Attempts to model this disorder using freely refining or rigidly hexagonal phenyl rings were unsuccessful, however. The BF_4^- anion is not disordered. All Cu, N, O and F atoms were refined anisotropically, and all hydrogen atoms were included in calculated positions.

Other measurements

Infra-red spectra were obtained as Nujol mulls pressed between KBr windows between 400–4000 cm^{-1} using a Perkin-Elmer Paragon 1000 spectrophotometer. UV/visible spectra were obtained with a Perkin-Elmer Lambda 12 spectrophotometer operating between 200–1100 nm, in 1 cm quartz cells. NMR spectra were run on a Bruker DPX250 spectrometer, operating at 250.1 MHz (^1H) and 62.9 MHz (^{13}C); low temperature ^1H spectra were obtained using a Bruker AM400 instrument operating at 400.1 MHz. Electron impact (EI) and positive ion fast atom bombardment (FAB; 3-NOBA matrix) mass spectra were performed on a Kratos MS890 spectrometer. Microanalyses were performed by the University of Cambridge Department of Chemistry microanalytical service. Melting points are uncorrected. X-band EPR spectra were obtained using a varian E103E instrument. All electrochemical measurements were carried out using an Autolab PGSTAT20 voltammetric analyser, in MeCN containing 0.1 M $Bu^n_4NPF_6$ (prepared from Bu^n_4NOH and HPF_6) as supporting electrolyte. Cyclic voltammetric experiments involved the use of a double platinum working/counter electrode and a silver wire reference electrode; all potentials quoted

Table 1. Experimental details for the single crystal structure determination of $[Cu(L^1)_2]BF_4$ (**I**)

Formula	$C_{32}H_{30}CuN_6O_4 \cdot BF_4$
M_r	712.97
Crystal habit	Yellow block
Crystal size (mm)	$0.45 \times 0.35 \times 0.30$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	15.244(3)
b (Å)	15.085(2)
c (Å)	14.135(5)
β (°)	92.94(2)
V (Å^3)	3246.1(14)
Z	4
No. of data for lattice parameters	25
θ range for lattice parameters (°)	$10.0 \leqslant \theta \leqslant 12.5$
T (K)	290(2)
Diffractometer	Rigaku AFC 7-R
Radiation	Graphite-monochromated Mo-K_α
λ (Å)	0.71069
Scan type	ω-2θ
Measured reflections	3861
Independent reflections	3033
R_{int}	0.13
Absorption correction	Semi-empirical (ψ-scans)
Min. transmission	0.87
Max. transmission	1.00
Observed reflections	1544
Criteria for observed	$I > 2\sigma(I)$
Range in 2θ (°)	$5 \leqslant 2\theta \leqslant 40$
Standards	3 every 200 reflections
Variation during data collection	2.7% decay
Range in h	$-14 \leqslant h \leqslant 14$
Range in k	$-14 \leqslant k \leqslant 1$
Range in l	$-1 \leqslant l \leqslant 13$
No. of parameters	272
No. of restraints	0
$R(F)^a$	0.065
$wR\,(F^2)^b$	0.202
GOF	1.008
Weighting scheme^c	$w = 1/[\sigma^2(F_o^2)+(0.0473P)^2+14.3394P]$
Max. shift/e.s.d.	0.009
$\Delta\rho_{\min}$ (e Å^{-3})	-0.31
$\Delta\rho_{\max}$ (e Å^{-3})	0.41

[a] $R = \Sigma[|F_o|\text{-}|F_c|]/\Sigma|F_o|$.

[b] $wR = [\Sigma w\,(F_o^2 - F_c^2)/\Sigma w F_o^4]^{1/2}$.

[c] $P = (F_o^2 + 2F_c^2)/3$.

in the text are referenced to an internal ferrocene/ferrocenium standard and were obtained at a scan rate of 100 mV/s. The number of electrons involved in a given voltammetric process was determined by comparison of the peak height in the CV with that of the $Fe^{II/III}$ couple shown by an equimolar amount of ferrocene.

RESULTS AND DISCUSSION

We have previously reported the synthesis of L^1 [1], *via* nucleophilic attack of the 3{5}–(2′,5′-dimethoxyphenyl)pyrazolide anion at 2-bromopyridine [6]. L^2 was prepared by an analogous reaction using the appropriate pyrazole precursor. Thus, reaction of the potassium salt of 3{5}-(3′,4′-dimethoxyphenyl)pyrazole [2] with 2-bromopyridine in diglyme, followed by an aqueous quench and recrystallisation from hot hexanes, yields white microcrystals of L^2 in *ca.* 70% yield. As we have previously observed for related ligands, attempts to confirm the regiochemistry of L^2 by NMR methods proved ambiguous. In particular, the magnitude of ${}^2J_{C^{3/5}\text{-}H^4}$ for L^2, which is 6.5 Hz in $CDCl_3$ solution, is intermediate between those ranges previously proposed as typical for 1,3- and 1,5- disubstituted pyrazoles [7]. However, this value is identical to those shown by L^1 and other 3-substituted 1-(pyrid-2-yl)pyrazoles we have prepared and crystallographically characterised [1,8,9]. In addition, this synthetic methodology is well known to produce exclusively the least sterically hindered pyrazole regioisomers [6]. Hence, although we have yet to crystallise free or complexed L^2, we are confident of its assignment as the 1,3-disubstituted isomer shown.

Complexation of $[\mathrm{Cu(NCMe)_4}]\mathrm{BF_4}$ by L^1 or L^2 in MeCN under N_2 rapidly affords yellow solutions, from which bright yellow microcrystalline solids can be isolated following concentration of the solution and addition of Et_2O. The IR spectra of all these complexes demonstrate the presence of BF_4^- and the appropriate bidentate ligand, while positive ion FAB mass spectrometry shows $[^{63}\mathrm{Cu(L)_2}]^+$ ($m/z = 625$) as the highest molecular ion. Hence, these products were formulated as the 4-coordinate complexes $[\mathrm{Cu(L)_2}]\mathrm{BF_4}$ ($L = L^1$, **I**; $L = L^2$, **II**), a conclusion confirmed by microanalysis. These $\mathrm{Cu^I}$ complexes are light stable, and can be stored in air at room temperature indefinitely as solids. However, solutions of **I** and **II** in MeCN, $MeNO_2$ or acetone oxidise slowly to their $\mathrm{Cu^{II}}$ congeners upon exposure to air.

The 250 MHz ^{1}H NMR spectra of **I** and **II** in CD_3CN or $\{CD_3\}_2CO$ at 293 K are paramagnetically broadened, suggesting the presence of trace $\mathrm{Cu^{II}}$ oxidation products in solution. In $\{CD_3\}_2CO$ at 400 MHz, however, the spectra slowly sharpen as the temperature is lowered, until at 233 K well resolved diamagnetic spectra were obtained for both compounds. This behaviour arises from the lower solubility of $[\mathrm{Cu(L)_2}](\mathrm{BF_4})_2$ ($L = L^1$, **III** [1]; $L = L^2$, **IV**, *vide infra*) in this solvent compared to **I** and **II**, so that lowering the temperature causes crystallisation from the solutions of the paramagnetic contaminants, which were observed as precipitates within the NMR tubes following their removal from the spectrometer. The low temperature NMR spectra of **I** and **II** contain the signals expected for a single ligand environment despite the potential for optical isomerism in these compounds, no decoalescence of the resonances from the dimethoxyphenyl protons being observed in these spectra down to 213 K. It is unclear whether this reflects a high rate of inversion between the Δ and Λ isomers [10], rapid rotation of the dimethoxyphenyl rings with respect to the rate of inversion, or simply insensitivity of the dimethoxyphenyl groups to the chirality at the Cu centres, however.

Weakly diffracting crystals were obtained by vapour diffusion of Et_2O into a MeCN solution of **I**. The solid state structure of the $[\mathrm{Cu(L^1)_2}]^+$ complex cation is shown in Fig. 1, while bond lengths and angles within the coordination sphere of the copper ion are listed in Table 2. The asymmetric unit contains one complex cation and anion, lying on a general position. Each L^1 ligand coordinates in bidentate fashion, with Cu—N bond lengths comparable to other $\mathrm{Cu^I}$ complexes of diimine chelates [11]. Interestingly, while the Cu(1)—N(2) and Cu(1)—N(9) distances are crystallographically indistinguishable (Table 2), the Cu(1)—N(30) bond length (2.110(8) Å) is markedly longer than Cu(1)—N(23) (2.011(8) Å). The coordination geometry at Cu(1) is somewhat distorted by the restricted bite angle of the chelating ligands, the average *intra*-ligand N—Cu—N angle being 80.4°. However, the dihedral angle between the planes defined by Cu(1) and the N-donors of the two ligands (θ) is 88.3(3)° (*c.f.* 90° for an "ideal" tetrahedron), while the average N—Cu(1)—N angle is 110.4°. The overall coordination geometry about Cu(1) is therefore close to tetrahedral. This is unusual for mononuclear $\mathrm{Cu^I}$ *bis*-diimine complexes, which usually

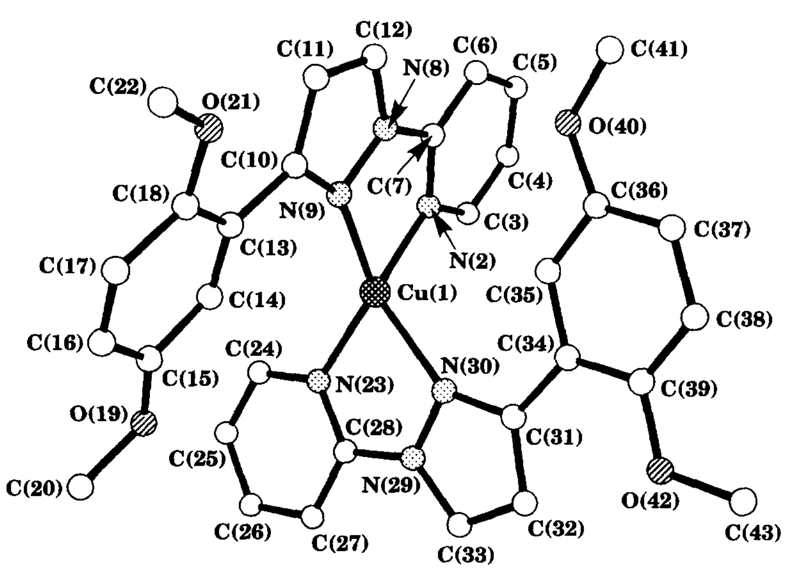

Fig. 1. Structure of the $[\mathrm{Cu(L^1)_2}]^+$ cation in the single crystal structure of **I**, showing the atom numbering scheme employed. For clarity, all hydrogen atoms have been omitted.

Table 2. Bond lengths (Å) and angles (°) at copper for $[Cu(L^1)_2]BF_4$ (**I**)

Cu(1)—N(2)	2.036(8)	Cu(1)—N(23)	2.011(8)
Cu(1)—N(9)	2.039(8)	Cu(1)—N(30)	2.110(8)
N(2)—Cu(1)—N(9)	80.6(3)	N(9)—Cu(1)—N(23)	133.5(3)
N(2)—Cu(1)—N(23)	124.7(4)	N(9)—Cu(1)—N(30)	123.6(3)
N(2)—Cu(1)—N(30)	120.0(3)	N(23)—Cu(1)—N(30)	80.1(3)

exhibit significant distortions towards planarity, examples with θ values in the solid state of between 49 and 89° having been reported [12,13].

The two coordinated ligands are almost planar: for ligand N(2)—C(22) the dihedral angles between the pyridine–pyrazole and pyrazole–phenyl least squares planes are 3.6(7) and 11.9(7)°, while for ligand N(23)—C(41) the corresponding angles are 6.0(6) and 8.4(6)°. There are no close Cu···O contacts within the complex, the closest Cu···O distance to each ligand being to the 5′-methoxy substituents (Cu(1)···O(19) = 4.616(10), Cu(1)···O(40) = 4.681(7) Å). However, the 6′ hydrogen atoms on each dimethoxyphenyl ring form a close contact to the Cu^+ ion (Cu(1)···C(14) = 3.370(11), Cu(1)···C(35) = 3.425(11) Å, which correspond to Cu(1)···H(14) = 2.62, Cu(1)···H(35) = 2.58 Å). It is possible that steric repulsions between Cu(1) and H(35), which would force this dimethoxyphenyl group away from the copper atoms, are the cause of the aforementioned asymmetry in the Cu—N bond lengths to this ligand.

There is no evidence for *intra*-molecular π-stacking between the dimethoxyphenyl pendants and pyridyl rings on adjacent ligands, as has been observed in some other Cu^I complexes of diimine ligands bearing aryl pendants [12]. However, there are weak *inter*-molecular graphitic interactions in the crystal lattice. The dimethoxyphenyl group of ligand N(2)—C(22) lies above the centre of the pyrazolylpyridine fragment of ligand N(2′)—C(22′), related to it by the transformation $-x$, $-y$, $-z$. The distance from the centroid of the C(13)—C(18) phenyl ring to the least squares plane of the N(2′)—C(12′) moiety is 3.78 Å, while the angle between the least squares planes of these two groups is 11.2(3)°. Similarly, the dimethoxyphenyl ring of ligand N(23)—C(43) forms a close contact with the pyridine ring of ligand N(23″)—C(43″), related by the transformation x, $1/2-y$, $1/2+z$, the corresponding interplanar distance and angle for this interaction being 3.30 Å and 12.9(3)°.

Feathery blue-violet needles of the Cu^{II} complex **IV** were prepared by complexation of $Cu(BF_4)_2 \cdot xH_2O$ ($x \approx 4$) by 2 molar equivalents of L^2 in MeCN, followed by concentration and vapour diffusion of Et_2O into the resultant mauve solution. IR, FAB mass spectrometry and microanalysis are all consistent with the expected formulation of $[Cu(L^2)_2](BF_4)_2$ (**IV**) for this product. Interestingly, solid **IV** is very different in appearance from the deep green complex **III** [1]. The UV/vis and X-band EPR spectra of **IV** in MeCN solution are consistent with a tetragonal $\{d_{x^2-y^2}\}^1$ Cu^{II} centre [14] (at 77 K $g_{\parallel} = 2.29$, $A_{\parallel}\,\{^{63,65}Cu\} = 144$ G, $g_{\perp} = 2.09$). However, **IV** is solvatochromic, forming solutions that are mauve in MeCN, dark green in $MeNO_2$ and khaki in acetone; diffusion of Et_2O in to all these solutions reforms **IV** as a blue-violet solid. In addition, pressing **IV** into a KBr disk for solid state UV/vis measurements results in coordination of Br^- to the complex [9]. Hence, while this solvent- and anion-sensitivity would be expected for a tetragonal Cu^{II} centre, it is impossible to draw detailed conclusions about the coordination geometry at Cu in **IV**, which we have been unable to crystallise in a form suitable for X-ray analysis, from spectroscopic measurements.

Reactions of $AgBF_4$ with 2 molar equivalents of L^1 or L^2 in $MeNO_2$ affords pale yellow solutions, which yield mildly photosensitive white microcrystalline products following concentration and addition of Et_2O. These compounds analyse as $[Ag(L)_2]BF_4$ ($L = L^1$, **V**; $L = L^2$, **VI**) and exhibit IR and UV/visible spectra that are barely distinguishable from those of their Cu^I analogues; **V** and **VI** were therefore formulated as mononuclear tetrahedral complexes of Ag^I. As for **I** and **II**, the ^1H NMR spectra of **V** and **VI** in $\{CD_3\}_2CO$ at 293 K showed peaks arising from a single ligand environment; low temperature measurements were not attempted, because these compounds would be expected to be more labile than their Cu^I analogues [10a]. Product **V** was also isolated from an analogous complexation reaction of L^1 with $AgBF_4$ in MeCN. However, treatment of $AgBF_4$ with 1 or 2 equivalents of L^2 under the same conditions gave a new photosensitive white product (**VII**) whose IR spectrum shows significant differences compared to those of **II** or **VI**. In particular, weak absorbances at 2284 and 2320 cm^{-1} in this spectrum suggest the presence of coordinated MeCN [15]. This proposition was supported by a ^1H NMR spectrum in CD_3NO_2, which, in addition to the peaks expected from coordinated L^2, showed a sharp singlet assignable to MeCN at 2.24 ppm, integrating to 3H against the L^2 aromatic resonances; and by microanalysis which was consistent with a formulation for **VII** of $[Ag(L^2)(NCMe)]BF_4$. Products **VI** and **VII** gave similar FAB mass spectra, however, both showing a highest molecular ion at $m/z = 669$, corresponding to $[^{107}Ag(L^2)_2]^+$. Compound **VII** was also isolated from a 1 : 1 complexation of $AgBF_4$ and L^2 in MeCN without a significant increase in yield with respect to Ag^+; a 1 : 1 reaction of L^1 with $AgBF_4$ in this solvent gave only reduced yields of **V**.

It is unclear how the molecular structure of **VII** differs from those of the other d^{10} complexes in this study. The simplest potential structure for **VII** is as a trigonal, mononuclear complex. However, given the well-known affinity of Ag^I for ether O-donor atoms, including aryl methoxy groups [16,17], it is also possible that L^2 might bridge between Ag^+ ions through the (potentially chelating) *ortho*-dimethoxyphenyl substituent to form an oligomeric structure in the solid state. In the absence of a crystal structure for **VII** we are unable to distinguish between these possibilities. We are similarly unable to rule out Ag—O coordination to the 2′-methoxy groups of L^1 in **V**, which would results in a 6-coordinate geometry at Ag^I similar to that observed at Cu^{II} in crystalline **III** [1].

The cyclic voltammogram (CV) of L^2 in MeCN/0.1 M $Bu^n_4NPF_6$ at 293 K shows an irreversible oxidation with a low-potential shoulder, centred at $Ep_a = +1.12$ V *vs* ferrocene/ferrocenium, with weak associated daughter products at $Ep_c = -0.67$ and -0.97 V. This process corresponds to the oxidation of the dimethoxyphenyl group in L^2 to a radical cation; for comparison, 1,2-dimethoxybenzene exhibits an analogous oxidation at $+1.45$ V *vs* SCE in this solvent [18] (*ca.* $+1.05$ V *vs* ferrocene/ferrocenium), while L^1 undergoes a *quasi*-reversible oxidation at $E_{1/2} = +0.93$ V [1]. It is known that 1,2-dialkoxybenzenes cleanly form cyclic trimers upon electrooxidation [19]; while this class of oxidation product should be disfavoured for L^2 because of the C—C bond to the pyrazole substituent, it is probable that the irreversibility of the $L^2/[L^2\cdot]^+$ couple arises from related recombination processes.

The CV of **I** under these conditions is identical to that we have previously described for **III** in the same solvent [1]. Hence, the following processes are observed: a *quasi*-reversible 2-electron oxidation wave at $E_{1/2} = +1.03$ V ($Ip_c : Ip_a = 0.3$, $\Delta Ep = 190$ mV at 100 mV s^{-1}), assigned as a $L^1/[L^1\cdot]^+$ oxidation centred on the pendant dimethoxyphenyl rings; a *quasi*-reversible (but chemically reversible) 1-electron couple at $E_{1/2} = +0.08$ V which is assignable to a $Cu^{I/II}$ oxidation; and an irreversible reduction at $Ep_c = -1.08$ V with an associated desorption spike attributable to a $Cu^{I/0}$ reduction. The CVs of **II** and **IV** are similarly indistinguishable: the L^2-based oxidation is an irreversible process, at $Ep_a = +1.24$ V; the $Cu^{I/II}$ couple is a broad, *quasi*-reversible but chemically reversible wave centred at $E_{1/2} = +0.10$ V; and the $Cu^{I/0}$ reduction appears at $Ep_c = -0.96$ V. The similarity of $E_{1/2}\{Cu^{I/II}\}$ for **III** and **IV** implies that the $Cu \cdots O$ contacts present in **III** [1] but not in **IV** have no effect on the relative stabilities of the $+2$ and $+1$ oxidation states in these complexes.

The CVs of the Ag^I complexes show ligand oxidations whose potentials and waveshapes are very similar to those of the uncomplexed ligands. For **V**, this process occurs at $E_{1/2} = +0.92$ V (Ip_c: $Ip_a = 0.25$), and exhibits low- and high-potential shoulders, while both **VI** and **VII** exhibit an irreversible wave with a low-potential shoulder at $Ep_c = +1.15$ V. This contrasts to **I–IV**, as well as with other complexes of L^1 we have studied [1], whose ligand-based oxidations are observed as a single peak with no fine structure. In addition, all three Ag^I products exhibit an irreversible reduction with an associated desorption spike at between $Ep_c = -0.25$ and -0.32 V, corresponding to an $Ag^{I/0}$ reduction; $AgBF_4$ exhibits this process at $Ep_c = -0.28$ V under these conditions. These data suggest that the only species present at the electrode in these samples are solvated Ag^+ and dissociated ligand, although whether these are also the predominant species in bulk MeCN solutions of the complexes is unclear.

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