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Synthesis, spectral characterization, properties and structures of copper(I) complexes containing novel bidentate iminopyridine ligands

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Abstract

Four new ligands, (4-methyl-phenyl)-pyridin-2-ylmethylene-amine (A), (2,3-dimethyl-phenyl)-pyridin-2-ylmethylene-amine (B), (2,4-dimethyl-phenyl)-pyridin-2-ylmethylene-amine (C) and (2,5-dimethyl-phenyl)-pyridin-2-ylmethylene-amine (D), and their corresponding copper(I) complexes, $[Cu(A)_2]ClO_4$ (**1a**), $[Cu(B)_2]ClO_4$ (**1b**), $[Cu(C)_2]ClO_4$ (**1c**), $[Cu(D)_2]ClO_4$ (**1d**), $[Cu(A)(PPh_3)_2]ClO_4$ (**2a**), $[Cu(B)(PPh_3)_2]ClO_4$ (**2b**), $[Cu(C)(PPh_3)_2]ClO_4$ (**2c**) and $[Cu(D)(PPh_3)_2]ClO_4$ (**2d**), have been synthesized and characterized by CHN analyses, ^1H and ^{13}C NMR, IR and UV–Vis spectroscopy. The crystal structures of $[Cu(B)_2]ClO_4$ (**1b**), $[Cu(C)_2]ClO_4$ (**1c**) and $[Cu(A)(PPh_3)_2]ClO_4 \cdot 1/2CH_3CN$ (**2a**) were determined from single crystal X-ray diffraction. The coordination polyhedron about the copper(I) center in the three complexes is best described as a distorted tetrahedron. A quasireversible redox behavior is observed for the complexes.

Keywords: 2-Pyridinecarbaldehyde; Diimine ligands; Copper(I) complexes; Distorted tetrahedral structure

1. Introduction

Monovalent copper (d^{10}) chemistry has drawn special attention because of its instability, unusual structural features, utility in solar energy and supramolecular devices, catalytic activity in photoredox reactions and the biological relevance of high potential copper complexes [1–8]. Most of the studies have been on four-coordinated tetrahedral Cu(I) complexes of the type $[Cu(LL)_2]^+$ or $[Cu(LL)(P)_2]^+$ where LL is a diimine and P is a phosphine, because of interdependence of their coordination geometry and their redox and photochemical behavior [9–12]. Recent reports have indicated that steric crowding and π-acidity in a well designed ligand are the most important prerequisites for the stability of copper(I) complexes and their redox, photophysical and photochemical behavior [13–16].

Although the coordination chemistry of symmetrical chelating diimines [e.g., 2,2-bipyridine, 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline] with copper(I) has been extensively studied [9,17–20], there are few data on complexes with unsymmetrical diimine ligands containing iminopyridine [21–26].

In a continuation of our work on the preparation of copper(I) diimine complexes with low lying MLCT transitions [27–29], here we report the synthesis and characterization of four ligands with extended conjugation, and their copper(I) complexes (Fig. 1). The structures, spectral properties and redox chemistry of these complexes are also discussed.

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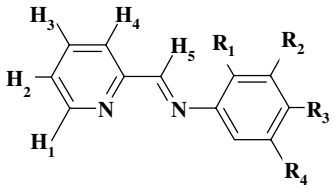

Ligand	R_1	R_2	R_3	R_4
A	H	H	CH_3	H
B	CH_3	CH_3	H	H
C	CH_3	H	CH_3	H
D	CH_3	H	H	CH_3

$[CuL_2]ClO_4$		$[CuL(PPh_3)_2]ClO_4$	
Complex	Ligand (L)	Complex	Ligand (L)
1a	A	**2a**	A
1b	B	**2b**	B
1c	C	**2c**	C
1d	D	**2d**	D

Fig. 1. Chemical formula of ligands (A–D), and Cu(I) complexes **1a**–**2d**.

2. Experimental

2.1. General

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

All chemicals used were reagent grade and used as received. Solvents used for the reactions were purified by literature methods [30]. $[Cu(CH_3CN)_4]ClO_4$ was prepared according to the literature procedure [31].

Elemental analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer. Infrared spectra were recorded on a Bruker Tensor 27 instrument. Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer; λ_{max} ($\log\varepsilon$). NMR spectra were obtained on a BRUKER AVANCE DRX500 (500 MHz) spectrometer. Proton chemical shifts are reported in part per million (ppm) relative to an internal standard of Me_4Si. All voltammograms were recorded with a three electrodes system consisting of an Ag/AgCl reference electrode, a platinum wire counter electrode, and Au as a working electrode. A Metrohm multipurpose instrument model 693 VA processor with 694A Va stand was used. In all electrochemical experiments the test solution was purged with argon gas for at least 5 min.

2.2. Synthesis

2.2.1. (4-Methyl-phenyl)-pyridin-2-ylmethylene-amine (A)

To a solution of pyridine-2-carbaldehyde (107 mg, 1 mmol) in 10 ml diethylether was added a solution of 4-methylaniline (107 mg, 1 mmol) in 10 ml diethylether and the resulting mixture was stirred for 2 h. The ligand (4-methyl-phenyl)-pyridin-2-ylmethylene-amine was obtained as a white microcrystalline precipitate. It was then filtered off, washed with cold diethylether, and dried in air. Yield: 172 mg (90%). IR (KBr): 1623 cm^{-1} ν(C=N). ^1H NMR (500 MHz, $CDCl_3$): 2.31 (s, 6H, $2CH_3$), 6.85–7.15 (m, 3H, ArH, amine ring), 7.32 (dd, 1H, $J_{H1,2} = 4.75$, $J_{H2,3} = 7.50$, H_2), 7.79 (*t*, 1H, $J_{H3,2} = 7.50$, $J_{H3,4} = 7.75$, H_3), 8.19 (d, 1H, $J_{H4,3} = 7.75$, H_4), 8.62 (s, 1H, H_5), 8.69 (d, 1H, $J_{H2,1} = 4.75$, H_1). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 21.04 ($^{13}CH_3$), 121.12, 121.74, 124.91, 129.85, 136.54, 136.69, 148.37, 149.63, 154.77, 159.62 (^{13}C=N). *Anal.* Calc. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.55; H, 6.17; N, 14.28%.

2.2.2. (2,3-Dimethyl-phenyl)-pyridin-2-ylmethylene-amine (B)

This ligand was prepared by a procedure similar to **1** using 121 mg (1 mmol) of 2,3-dimethylaniline. Yield: 190 mg (90%). IR (KBr): 1630 cm^{-1} ν(C=N). ^1H NMR (500 MHz, $CDCl_3$): 2.31 (s, 6H, $2CH_3$), 6.85–7.15 (m, 3H, ArH, amine ring), 7.32 (dd, 1H, $J_{H1,2} = 4.12$, $J_{H2,3} = 7.30$, H_2), 7.76 (*t*, 1H, $J_{H3,2} = 7.30$, $J_{H3,4} = 7.90$, H_3), 8.24 (d, 1H, $J_{H4,3} = 7.90$, H_4), 8.50 (s, 1H, H_5), 8.68 (d, 1H, $J_{H2,1} = 4.12$, H_1). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 13.90 (3-$^{13}CH_3$), 21.12 (2-$^{13}CH_3$), 115.43, 121.62, 124.98, 126.16, 127.98, 130.77, 136.58, 137.56, 149.56, 150.10, 155.01, 159.77 (^{13}C=N). *Anal.* Calc. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.99; H, 6.70; N, 13.35%.

2.2.3. (2,4-Dimethyl-phenyl)-pyridin-2-ylmethylene-amine (C)

This ligand was prepared by a procedure similar to **1** using 121 mg (1 mmol) of 2,4-dimethylaniline. Yield: 185 mg (88%). IR (KBr): 1629 cm^{-1} ν(C=N). ^1H NMR ($CDCl_3$; δ): 2.33 (s, 3H, 4-CH_3), 2.37 (s, 3H, 2-CH_3), 6.93–7.05 (m, 3H, ArH, amine ring), 7.33 (dd, 1H, $J_{H1,2} = 4.5$, $J_{H2,3} = 7.50$, H_2), 7.76 (*t*, 1H, $J_{H3,2} = 7.50$, $J_{H3,4} = 8.00$, H_3), 8.24 (d, 1H, $J_{H4,3} = 8.00$, H_4), 8.50 (s, 1H, H_5), 8.68 (d, 1H, $J_{H2,1} = 4.12$, H_1). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 17.78 (4-$^{13}CH_3$), 20.96 (2-$^{13}CH_3$), 117.28, 121.54, 124.86, 127.3, 131.21, 132.49, 136.26, 136.55, 147.43, 149.53, 155.08, 159.03 (^{13}C=N). *Anal.* Calc. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.96; H, 6.70; N, 13.35%.

2.2.4. (2,5-Dimethyl-phenyl)-pyridin-2-ylmethylene-amine (D)

This ligand was prepared by a procedure similar to **1** using 121 mg (1 mmol) of 2,5-dimethylaniline. Yield:

200 mg (95%). IR (KBr): 1629 cm^{-1} ν(C=N). ^1H NMR ($CDCl_3$; δ): 2.34 (s, 3H, $2CH_3$), 6.83–7.13 (m, 3H, ArH, amine ring), 7.34 (dd, 1H, $J_{H1,2} = 4.8$, $J_{H2,3} = 7.65$, H_2), 7.79 (*t*, 1H, $J_{H3,2} = 7.65$, $J_{H3,4} = 7.90$, H_3), 8.24 (d, 1H, $J_{H4,3} = 7.90$, H_4), 8.50 (s, 1H, H_5), 8.69 (d, 1H, $J_{H2,1} = 4.80$, H_1). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 17.70 (5-$^{13}CH_3$), 20.99 (2-$^{13}CH_3$), 118.31, 121.57, 124.97, 127.09, 129.08, 130.25, 136.35, 136.60, 149.50, 149.92, 154.91, 159.59 (^{13}C=N). *Anal.* Calc. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.96; H, 6.70; N, 13.34%.

2.2.5. *[Cu^I(A)$_2$]ClO$_4$ (**1a**)*

To a stirring solution of (4-methyl-phenyl)-pyridin-2-ylmethylene-amine, A (19.6 mg, 0.1 mmol) in 5 ml acetonitrile was added $[Cu(CH_3CN)_4]ClO_4$ (16.4 mg, 0.05 mmol) in 5 ml acetonitrile and the resulting mixture was stirred for 10 min. The solution turned dark red rapidly. The volume of the solvent was reduced under vacuum to about 4 ml. The diffusion of diethyl ether vapor into the concentrated solution gave dark-red crystals. The resulting crystals were filtered off, washed with a mixture of diethylether–acetonitrile (9:1 v/v), and dried under vacuum. Yield: 25 mg (92%). IR (KBr): 1582 cm^{-1} ν(C=N), 1090 cm^{-1} ν(Cl–O). ^1H NMR ($CDCl_3$; δ): 2.28 (s, 3H, CH_3), 7.09–7.40 (m, 4H, ArH, amine ring), 7.60 (*t*, 1H, H_2), 8.04–8.21 (m, 2H, H_3, H_4), 8.48 (d, 1H, $J_{H2,1} = 4.0$, H_1), 9.20 (s, 1H, H_5). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 21.10 ($^{13}CH_3$), 118.21, 122.48, 123.49, 128.60, 130.40, 131.25, 138.47, 139.93, 144.05, 149.09, 151.28, 156.28 (^{13}C=N). *Anal.* Calc. for $C_{26}H_{24}ClCuN_4O_4$: C, 56.22; H, 4.35; N, 10.09. Found: C, 56.23; H, 4.34; N, 10.10%.

2.2.6. *[Cu^I(B)$_2$]ClO$_4$ (**1b**)*

This complex was prepared by a procedure similar to **1a** using 21 mg (0.1 mmol) of (2,3-dimethyl-phenyl)-pyridin-2-ylmethylene-amine, B. Dark-red crystals were collected by filtration and dried *in vacuo*. Yield: 27 mg (93%). IR (KBr): 1578 cm^{-1} ν(C=N), 1095 cm^{-1} ν(Cl–O). ^1H NMR ($CDCl_3$; δ): 2.03 (s, 3H, 3-CH_3), 2.22 (s, 3H, 2-CH_3), 6.58–7.06 (m, 3H, ArH, amine ring), 7.74 (*t*, 1H, H_2), 7.98–8.12 (m, 2H, H_3, H_4), 8.59 (s, 1H, H_5), 8.65 (d, 1H, $J_{H2,1} = 4.5$, H_1). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 14.90 (3-$^{13}CH_3$), 20.12 (2-$^{13}CH_3$), 116.52, 122.01, 126.98, 127.14, 128.08, 132.78, 136.58, 138.56, 150.50, 154.12, 156.32, 159.90 (^{13}C=N). *Anal.* Calc. for $C_{28}H_{28}ClCuN_4O_4$: C, 57.63; H, 4.84; N, 9.60. Found: C, 57.62; H, 4.86; N, 9.61%.

2.2.7. *[Cu^I(C)$_2$]ClO$_4$ (**1c**)*

This complex was prepared by a procedure similar to **1a** using 21 mg (0.1 mmol) of (2,4-dimethyl-phenyl)-pyridin-2-ylmethylene-amine, C. Dark-red crystals were collected by filtration and dried *in vacuo*. Yield: 25 mg (86%). IR (KBr): 1585 cm^{-1} ν(C=N), 1090 cm^{-1} ν(Cl–O). ^1H NMR ($CDCl_3$; δ): 2.09 (s, 3H, 4-CH_3), 2.28 (s, 3H, 2-CH_3), 6.69-6.91 (m, 3H, ArH, amine ring), 7.68 (*t*, 1H, H_2), 8.01–8.11 (m, 2H, H_3, H_4), 8.54 (d, 1H, $J_{H2,1} = 4.75$, H_1), 8.60 (s, 1H, H_5). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 17.80 (4-$^{13}CH_3$), 20.90 (2-$^{13}CH_3$), 120.54, 127.65, 128.14, 128.88, 130.57, 131.66, 137.67, 138.53, 154.52, 149.21, 150.47, 159.91 (^{13}C=N). *Anal.* Calc. for $C_{28}H_{28}ClCuN_4O_4$: C, 57.63; H, 4.84; N, 9.60. Found: C, 57.62; H, 4.85; N, 9.59%.

2.2.8. *[Cu^I(D)$_2$]ClO$_4$ (**1d**)*

This complex was prepared by a procedure similar to **1a** using 21 mg (0.1 mmol) of (2,5-dimethyl-phenyl)-pyridin-2-ylmethylene-amine, D. Dark-red crystals were collected by filtration and dried *in vacuo*. Yield: 26 mg (89%). IR (KBr): 1590 cm^{-1} ν(C=N), 1091 cm^{-1} ν(Cl–O). ^1H NMR ($CDCl_3$; δ): 2.05 (s, 3H, 3-CH_3), 2.12 (s, 3H, 2-CH_3), 6.50–7.16 (m, 3H, ArH, amine ring), 7.65 (*t*, 1H, H_2), 7.99–8.10 (m, 2H, H_3, H_4), 8.59 (s, 1H, H_5), 8.68 (d, 1H, $J_{H2,1} = 4.5$, H_1). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 13.85 (5-$^{13}CH_3$), 20.10 (2-$^{13}CH_3$), 116.86, 122.21, 125.98, 126.18, 128.17, 131.70, 135.49, 139.01, 151.10, 153.99, 156.88, 160.00 (^{13}C=N). *Anal.* Calc. for $C_{28}H_{28}ClCuN_4O_4$: C, 57.63; H, 4.84; N, 9.60. Found: C, 57.62; H, 4.83; N, 9.59%.

2.2.9. *[Cu^I(A)(PPh$_3$)$_2$]ClO$_4$ (**2a**)*

To a 3 ml MeCN solution of $[Cu(CH_3CN)_4]ClO_4$ (32.8 mg, 0.1 mmol), 2 equivalent of Ph_3P (52.2 mg, 0.2 mmol) were added, and the solution was stirred for 15 min. The solvent was evaporated under vacuum at room temperature. The dry product $[Cu(CH_3CN)_2(PPh_3)_2]ClO_4$ was added to a stirring solution of 19.6 mg (0.1 mmol) pyridin-2-ylmethylene-p-tolyl-amine, A, in 3 ml MeCN. The solution rapidly turned yellow and it was stirred for 20 min at room temperature. The reaction medium was concentrated under vacuum, until the first crystals appeared in the liquid phase. Bright-yellow crystals were obtained by diffusion of Et_2O vapor into the concentrated solution. Yield: 80 mg (91%). IR (KBr): 1580 cm^{-1} ν(C=N), 1092 cm^{-1} ν(Cl–O), ^1H NMR (500 MHz, $CDCl_3$): ^1H NMR ($CDCl_3$; δ): 2.33 (s, 3H, CH_3), 6.96–7.40 (m, 35H, ArH, amine ring, PPh_3), 8.04 (m, 2H, H_3, H_4), 8.38 (d, 1H, $J_{H2,1} = 7.5$, H_1), 9.01 (s, 1H, H_5). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 21.1 ($^{13}CH_3$), 122.71, 126.25, 127.59, 128.32 (d, $J = 4.2$, *ipso*-C of PPh_3), 128.94, 130.04, 130.32, 133.15, 138.48, 139.55, 148.70, 149.12, 150.12, 162.69 (^{13}C=N). *Anal.* Calc. for $C_{49}H_{42}ClCuN_2O_4P_2$: C, 66.59; H, 4.79; N, 3.17. Found: C, 66.58; H, 4.80; N, 3.16%.

2.2.10. *[Cu^I(B)(PPh$_3$)$_2$]ClO$_4$ (**2b**)*

This complex was prepared by a procedure similar to **1** using 21 mg (1 mmol) of (2,3-dimethyl-phenyl)-pyridin-2-ylmethylene-amine, B. Yellow-orange crystals were collected by filtration and dried *in vacuo*. Yield: 70 mg (79%). IR (KBr): 1591 cm^{-1} ν(C=N), 1088 cm^{-1} ν(Cl–O), ^1H NMR (500 MHz, $CDCl_3$): ^1H NMR ($CDCl_3$; δ): 1.55 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 6.74–7.39 (m, 34H, ArH, amine ring, PPh_3), 7.53 (*t*, 1H, H_2), 8.23 (m, 2H, H_3, H_4), 8.42 (d, 1H, $J_{H2,1} = 7.75$, H_1), 8.60 (s, 1H, H_5). ^{13}C {^1H} NMR (500 MHz, $CDCl_3$): 14.12 (4-$^{13}CH_3$), 21.1 (2-$^{13}CH_3$), 119.45, 126.02, 127.50, 128.47 (d, $J = 4.2$,

ipso-C of PPh3), 128.94, 130.24, 130.38, 133.14, 138.57, 139.87, 148.77, 149.66, 150.08, 162.98 (^{13}C=N). *Anal.* Calc. for $C_{50}H_{44}ClCuN_2O_4P_2$: C, 66.89; H, 4.94; N, 3.12. Found: C, 66.87; H 4.95; N, 3.11%.

2.2.11. $[Cu^{I}(C)(PPh_3)_2]ClO_4$ (**2c**)

This complex was prepared by a procedure similar to **1** using 21 mg (0.1 mmol) of (2,4-dimethyl-phenyl)-pyridin-2-ylmethylene-amine, C. Yellow-orange crystals were collected by filtration and dried *in vacuo*. Yield: 80 mg (90%). IR (KBr): 1595 cm^{-1} ν(C=N), 1091 cm^{-1} ν(Cl–O), ^{1}H NMR (500 MHz, $CDCl_3$): 1.45 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 6.70–7.59 (m, 34H, ArH, amine ring, PPh_3), 7.50 (*t*, 1H, H_2), 8.20 (m, 2H, H_3, H_4), 8.41 (d, 1H, $J_{H2,1} = 7.8$, H_1), 8.63 (s, 1H, H_5). ^{13}C {^{1}H} NMR (500 MHz, $CDCl_3$): 18.35 (4-$^{13}CH_3$), 20.30 (2-$^{13}CH_3$), 123.60, 124.30, 126.63, 128.28 (d, $J = 4.0$, *ipso*-C of PPh_3), 129.12, 130.56, 132.32, 133.23, 137.60, 139.12, 147.91, 149.56, 150.24, 162.55 (^{13}C=N). *Anal.* Calc. for $C_{50}H_{44}ClCuN_2O_4P_2$: C, 66.89; H, 4.94; N, 3.12. Found: C, 66.88; H, 4.95; N, 3.12%.

2.2.12. $[Cu^{I}(D)(PPh_3)_2]ClO_4$ (**2d**)

This complex was prepared by a procedure similar to **1** using 21 mg (0.1 mmol) of (2,5-dimethyl-phenyl)-pyridin-2-ylmethylene-amine, D. Yellow-orange crystals were collected by filtration and dried *in vacuo*. Yield: 75 mg (84%). IR (KBr): 1590 cm^{-1} ν(C=N), 1091 cm^{-1} ν(Cl–O), ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR ($CDCl_3$; δ): 1.68 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 6.90–7.40 (m, 34H, ArH, amine ring, PPh_3), 7.53 (*t*, 1H, H_2), 8.24 (m, 2H, H_3, H_4), 8.43 (d, 1H, $J_{H2,1} = 7.25$, H_1), 8.63 (s, 1H, H_5). ^{13}C {^{1}H} NMR (500 MHz, $CDCl_3$): 17.30 (5-$^{13}CH_3$), 20.54 (2-$^{13}CH_3$), 123.00, 125.55, 127.84, 128.42 (d, $J = 4.1$, *ipso*-C of PPh3), 128.99, 130.40, 131.42, 133.12, 136.58, 139.87, 148.15, 149.64, 150.14, 162.70 (^{13}C=N). *Anal.* Calc. for $C_{50}H_{44}ClCuN_2O_4P_2$: C, 66.89; H, 4.94; N, 3.12. Found: C, 66.90; H, 4.93; N, 3.11%.

2.3. X-ray analysis

Crystals of **1b**, **1c** and **2a** suitable for X-ray analysis were obtained as described above. The single crystals were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo Kα $\lambda = 0.71073$ Å). The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software [32]. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97. The crystal data and refinement details are summarized in Table 1.

Table 1
Crystal data and single crystal X-ray diffraction refinement details for compounds **1b**, **1c** and **2a**

Formula	$C_{28}H_{28}ClCuN_4O_4$	$C_{28}H_{28}ClCuN_4O_4$	$C_{100}H_{87}Cl_2Cu_2N_5O_8P_4$
Formula weight	583.53	583.53	1808.61
Crystal system	monoclinic	monoclinic	triclinic
Space group	*P*2/*n*	*C*2/*c*	$P\bar{1}$
a (Å)	12.350(4)	34.062(5)	11.0500(10)
b (Å)	8.238(3)	8.938(2)	12.676(2)
c (Å)	13.201(4)	22.760(5)	32.847(5)
α (°)	90.00	90.00	79.13(5)
β (°)	91.348(2)	128.33(5)	81.31(4)
γ (°)	90.00	90.00	85.21(7)
V (A^3)	1342.7(8)	5435.6(42)	4459.3(14)
Z	2	8	2
Density (g cm^{-3})	1.443	1.426	1.347
μ(Mo Kα) (mm^{-1})	0.954	0.943	0.669
F(000)	604	2416	1876
Data collection			
Temperature (K)	173(2)	173(2)	173(2)
θ minimum–maximum	2.91–30.02	1.52–27.45	1.27–27.49
Dataset [*h*,*k*,*l*]	−17/11, −11/11, −18/18	−43/44, −11/10, −25/29	−9/14, −16/16, −42/42
Total, unique data, R_{int}	3920, 2479, 0.0503	6206, 3739, 0.0955	19 850, 10 524, 0.0956
Observed data	>2σ(*I*)	>2σ(*I*)	>2σ(*I*)
Refinement			
No. of reflections, no. of parameters	3920, 173	6207, 370	19 850, 1075
R_1, R_2	0.0437, 0.0892	0.0685, 0.1877	0.0860, 0.1931
wR_1, wR_2	0.0994, 0.1126	0.1526, 0.1963	0.1809, 0.2144
Goodness-of-fit	1.078	1.040	1.070
Maximum and average shift/error	0.001, 0.000	0.003, 0.000	0.002, 0.000
Minimum, maximum resolved density (e/A^3)	−0.484, 0.390	−0.708, 0.696	−1.403, 1.518

3. Results and discussion

3.1. General characterization

The IR spectra of the free ligands exhibit the characteristic band of the imine group, which appears in the region 1623–1630 cm^{-1}. This band is shifted to lower frequencies in the IR spectra of the corresponding complexes due to the coordination of the imine nitrogen [33], and appears in the region 1580–1595 cm^{-1}. A strong band at about 1085 cm^{-1} in the IR spectra of the complexes is characteristic of the asymmetric Cl–O stretching mode of the perchlorate anion [34].

The electronic absorption spectra of the ligands and the corresponding complexes are presented in Table 2. Since no d–d transitions are expected for a d^{10} complex, the UV–Vis bands are assigned to metal to ligand charge transfer (MLCT) or ligand-centered $\pi \rightarrow \pi^*$ transitions [35].

The absorption spectrum of $[Cu(A)_2]ClO_4$ (**1a**), in chloroform features a band with a true maximum at 518 nm, whereas $[Cu(A)(PPh_3)_2]ClO_4$ (**2a**), shows a clear shoulder at 419 nm, which is shifted considerably (ca. 99 nm) relative to that of complex **1a**. A similar shift (90 nm) has been reported in going from $[Cu(dmp)_2]^+$ ($\lambda_{MLCT} = 454$ nm) to $[Cu(dmp)(PPh_3)_2]^+$ ($\lambda_{MLCT} = 365$ nm) [36] and also similar shifts were observed in the other $Cu(L)_2^+$ complexes **1b**–**1d** relative to the $Cu(L)(PPh_3)_2^+$ complexes **2b**–**2d** (Table 2).

The considerable red shift in the position of the first MLCT band of complexes **1a**–**1d** as compared to that of other bis(diimine) copper(I) complexes is quite interesting and points to the possible application of these complexes as more efficient charge transfer photosensitizers in the visible region. Additional absorption bands are also observed in the spectra of **1a**–**2d** in chloroform in the UV region (Table 2). The intensity of these bands are consistent with being assigned as ligand-centered $\pi \rightarrow \pi^*$ or/and charge-transfer transitions.

The ^1H NMR spectra and peak assignments are presented in the experimental section in each complex. These peaks are assigned based on the splitting of the resonance signals, spin coupling constants and the literature, and are clearly in accordance with the molecular structure determined by X-ray crystal structure analysis. The ^1H resonances of the coordinated ligands are commonly observed in complexes **1a**–**2d**. In complexes **2a**–**2d**, however, the aromatic H atoms of the coordinated Ph_3P ligands overlap to some extent with those of the phenyl H atoms of ligands A–D. Aside from the aromatic H-atoms, which appear at 7.00–8.15 ppm in the complexes, the imine protons appear as a singlet at 8.60–9.50 ppm in the complexes. The downfield shift of the iminic protons relative to the free ligands can be attributed to the deshielding effect resulting from the coordination of the ligands [29]. The singlet at about 2 ppm in the compounds is assigned to the CH_3 substitutions of the phenyl ring.

The sharp NMR peaks are indicative of diamagnetic Cu(I) complexes. The appearance of a unique signal for each type of proton in $CDCl_3$ solution indicates that the symmetry of the molecules is retained in solution, and only one isomer or exchange processes within the NMR timescale are present.

3.2. X-ray structures of $[Cu(B)_2]ClO_4$ (**1b**), $[Cu(C)_2]ClO_4$ (**1c**) and $[Cu(A)(PPh_3)_2]ClO_4 \cdot 1/2CH_3CN$ (**2a**)

The crystallographic data are summarized in Table 1 and selected bond distances and angles are given in Table 3. No classical H-bonding occurs in these three crystal structures.

A view of the cation of complex **1b**, including the atom-numbering scheme is illustrated in Fig. 2. While a tetrahedral geometry might be expected for a four coordinated copper(I) center, the coordination sphere around the metal ion in this complex is distorted by the restricting bite angles of the chelating ligand. The intraligand N1–Cu–N2 angle is much less than 109.5°, being only 81.07(7)°. On the contrary the N2–Cu–N2b and N1–Cu–N2b angles (134.31(10)°, 122.41(7)°) are much larger than those of a tetrahedral complex. The average Cu–N bond distance (2.037 Å) is similar to that found in the $[Cu(dpdmp)_2]^+$ cation (2.047 Å) at room temperature [37], and other Cu(I) pseudotetrahedral complexes (typical $Cu–N_{av} = 2.055$ Å) [38].

Table 2
IR, UV–Vis spectral data and cyclic voltammetric data of ligands and complexes

Compound	ν(C=N)/cm^{-1}	ν(Cl–O)/cm^{-1}	λ_{max}/nm (Log ε/M^{-1} cm^{-1})	E_p^a	E_p^c
A	1623		241 (4.05), 283 (3.97), 329 (3.92)		
B	1630		245 (4.29), 281 (4.20), 332 (3.90)		
C	1629		239 (4.68), 275 (4.58), 341 (4.44)		
D	1629		241 (4.86), 273 (4.75), 339 (4.45)		
1a	1582	1090	249 (4.52), 339 (4.55), 518 (3.74)	0.41	0.84
1b	1578	1095	255 (4.49), 328 (4.17), 500 (3.59)	0.46	0.67
1c	1585	1090	248 (4.54), 341 (4.23), 500 (3.61)	0.46	0.66
1d	1580	1091	254 (4.37), 315 (4.08), 485 (3.51)	0.48	0.67
2a	1580	1092	243 (4.09), 342 (4.37), 419 (4.01)	0.29	1.73
2b	1591	1088	243 (4.53), 273 (4.41), 414 (3.54)	0.41	1.71
2c	1595	1091	241 (4.60), 275 (4.31), 418 (3.65)	0.39	1.69
2d	1590	1091	243 (4.66), 268 (3.57), 414 (3.72)	0.37	1.68

Table 3
Selected bond lengths (Å) and bond angles ° for **1b**, **1c** and **2a**

1b		**1c**		**2a**			
				I		II	
Cu–N1	2.0180(16)	Cu1–N1	2.021(4)	Cu1–N1	2.064(4)	Cu2–N3	2.085(6)
Cu–N2	2.0564(16)	Cu1–N2	2.067(4)	Cu1–N2	2.103(5)	Cu2–N4	2.142(5)
Cu–N1b	2.0179(16)	Cu1–N3	2.039(4)	Cu1–P1	2.2447(18)	Cu2–P3	2.2359(19)
N1–C1	1.279(2)	Cu1–N4	2.018(4)	Cu1–P2	2.2489(19)	Cu2–P4	2.275(2)
N1–C7	1.439(3)	N2–C1	1.283(6)	N1–C5	1.438(6)	N3–C54	1.407(8)
C1–C2	1.460(3)	N2–C7	1.427(6)	N1–C8	1.285(7)	N3–C57	1.320(8)
		N4–C15	1.284(6)	N2–C9	1.343(7)	N4–C58	1.346(9)
		N4–C21	1.427(6)	N2–C13	1.349(7)	N4–C62	1.330(9)
		C1–C2	1.453(7)	C8–C9	1.456(8)	C57–C58	1.417(10)
		C2–C3	1.386(7)	P1–C14	1.825(6)	P3–C75	1.830(7)
N1–Cu–N2	81.07(7)	N1–Cu1–N2	82.06(17)	N1–Cu–N2	79.39(18)	N3–Cu–N4	79.6(2)
N1–Cu–N1b	121.27(10)	N1–Cu1–N3	125.27(16)	N1–Cu–P1	118.13(14)	N3–Cu–P3	120.04(15)
N1–Cu–N2b	122.41(7)	N1–Cu1–N4	126.21(18)	N1–Cu–P2	114.76(13)	N3–Cu–P4	104.66(14)
N2–Cu–N2b	134.31(10)	N2–Cu1–N3	105.68(17)	N2–Cu–P1	105.35(14)	N4–Cu–P3	115.11(15)
Cu–N1–C1	113.79(14)	N2–Cu1–N4	140.10(16)	N2–Cu–P2	111.81(13)	N4–Cu–P4	98.79(14)
Cu–N1–C7	126.23(11)	N3–Cu1–N4	81.65(17)	P1–Cu–P2	119.22(7)	P3–Cu–P4	126.99(8)
Cu–N2–C2	111.30(13)	Cu1–N1–C2	111.3(4)	Cu1–N1–C5	126.1(3)	Cu2–N3–C54	128.7(4)
Cu–N2–C6	131.61(13)	Cu1–N1–C6	130.2(4)	Cu1–N1–C8	113.9(4)	Cu2–N3–C57	112.2(5)
C1–N1–C7	119.97(16)	Cu1–N2–C1	110.3(3)	Cu1–N2–C9	112.0(4)	Cu2–N4–C58	110.1(5)
C2–N2–C6	117.08(16)	Cu1–N2–C7	126.1(3)	Cu1–N2–C13	129.7(4)	Cu2–N4–C62	131.1(6)
		C1–N2–C7	119.3(4)	C5–N1–C8	119.4(5)	C54–N3–C57	119.1(6)
		C2–N1–C6	118.3(5)	C9–N2–C13	118.2(5)	C58–N4–C62	118.0(7)

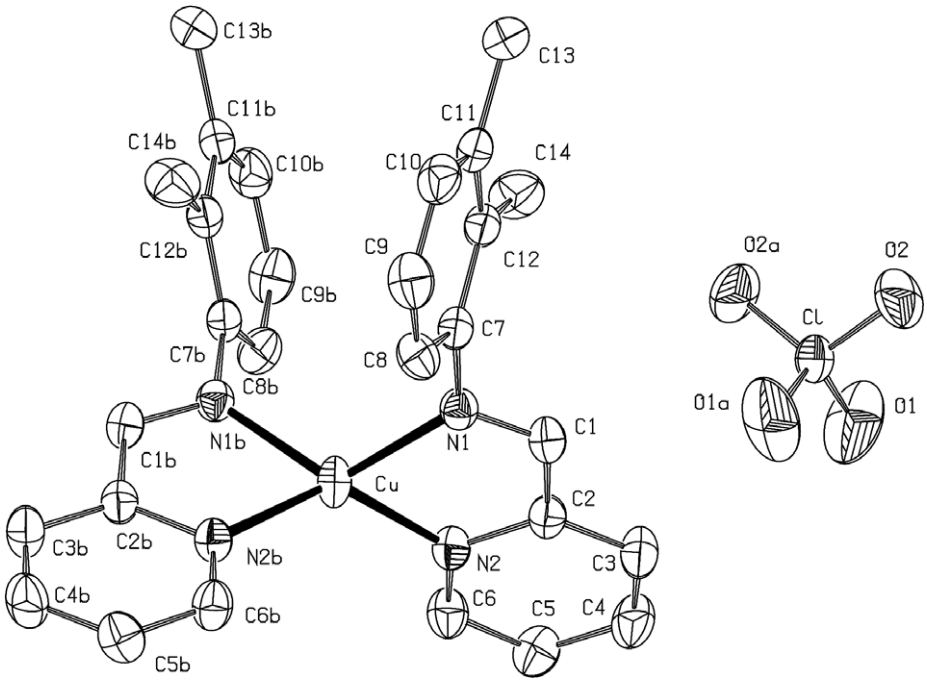

Fig. 2. ORTEP view of the crystal structure of $[Cu(B)_2]ClO_4$ (**1b**) showing the atom labelling scheme. The thermal ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

The dihedral angle between the two chelate rings is 85(1)°. The value for the dihedral angle of N1–C1–C2–N2 is 0.00(3)°, and comparison of the dihedral angles between the chelate rings and pyridine groups indicate the coplanarity of these moieties, resulting in a bite size of 3.233 Å of d(N(1)–N(2)) for the chelating ligand. The environment of the imine and pyridine nitrogen atoms is planar. The planarity is measured by three N atom bond angles ($\sum$N). For **1b**, the sum of these angles is 359.99° for N1 and N2. Despite the fact that the nitrogen atoms in **1b** are sp^2 hybridized, some strain in the chelate ring is suggested by the deviation from the 120° angle about the

nitrogen, Cu–N1–C1 (113.79(14)°), Cu–N1–C7 (126.23(11)°), C1–N1–C7 (119.97(16)°), Cu–N2–C2 (111.30(13)°), Cu–N2–C6 (131.61(13)°) and C2–N2–C6 (117.08(16)°). The dihedral angle of the chelate ring and phenyl ring (C7 → C12) is 69.4(3)°.

The cation of complex **1c**, along with the atom-numbering scheme, is shown in Fig. 3. As in complex **1b**, the geometry about Cu(I) in **1c** is also distorted by the restricting bite angles of the chelating ligand. The N1–Cu1–N2 and N3–Cu1–N4 angles are 82.1(2)° and 81.7(2)°, respectively. However, the N2–Cu1–N4, N1–Cu1–N4 and N1–Cu1–N3 angles are 140.0(2)°, 126.3(2)° and 125.3(2)° respectively.

The average Cu–N bond distance (2.0375 Å) is similar to that found in other Cu(I)(diimine) pseudotetrahedral complexes [37–39].

The dihedral angle between the two chelate rings is 83(1)°. Torsion angles in the chelating rings and the pyridine groups are listed in Table 4. This result demonstrates that the chelating rings are nearly planar and the pyridine groups are coplanar with the chelate rings. Despite the fact that the chelate ring are planar, the sum of three N atom bond angles is 359.4° for N1, 359.9 for N2, 360 for N3, and 359.3 N4, however, some strain in the chelate ring is suggested by the deviation from the 120° angle about the nitrogen, for example; Cu1–N1–C6 (130.2(4)°), Cu1–N2–C7 (126.3(4)°) and Cu1–N3–C20 (130.2(4)°). The planarity of the chelate rings results in a bite size of 3.233 Å for d(N(1)–N(2)) and 3.248 for d(N(3)–N(4)) for the two chelating ligands.

The cation of complex **2a**, along with the atom-numbering scheme, is shown in Fig. 4, and selected bond distances and angles are listed in Table 3. The compound **2a** crystallizes with two molecules per asymmetric unit, probably due to some small conformational differences. As in complex **1b** and **1c**, the coordination environment around the metal ion in this complex is pseudotetrahedral with large angular distortion arising from the low intraligand N1–Cu–N2 chelate angle, 79.39(18)° in I and N3–Cu–N4 chelate angle, 79.6(2)° in II. However, the P1–Cu–P2, 119.22(7)° angle in I and the P3–Cu–P4, 126.99(8)° angle in II have opened

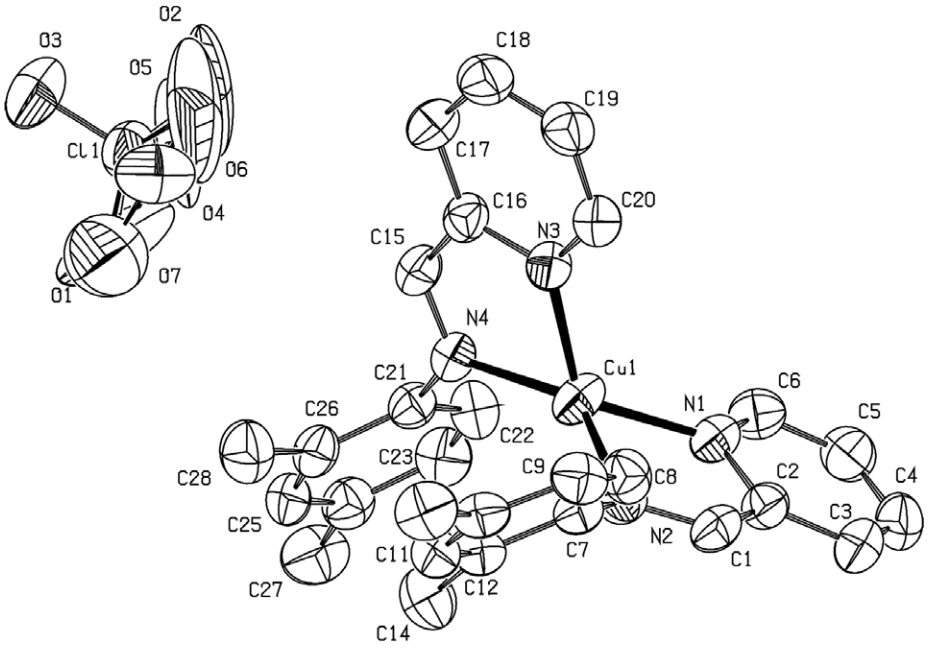

Fig. 3. ORTEP view of the crystal structure of $[Cu(C)_2]ClO_4$ (**1c**) showing the atom labelling scheme. The thermal ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity.

Table 4
Torsion angles for chelating rings

1b		**1c**		**2a**			
				I		II	
N1–C1–C2–N2	0.0(3)	N2–C1–C2–N1	−12.8(7)	N1–C8–C9–C10	174.4(5)	N3–C57–C58–N4	4.2(9)
N1–C1–C2–C3	178.3(2)	N2–C1–C2–C3	169.1(5)	N1–C8–C9–C10	174.4(5)	N3–C57–C58–C59	−171.4(6)
Cu–N1–C1–C2	3.6(3)	Cu1–N1–C2–C1	4.3(5)	Cu1–N1–C8–C9	4.1(6)	Cu2–N3–C57–C58	0.1(7)
C1–C2–C3–C4	−177.0(2)	C1–C2–C3–C4	−179.2(5)	C1–C2–C3–C4	179.8(6)	C57–C58–C59–C60	175.9(7)
Cu–N2–C2–C1	−3.4(2)	Cu1–N2–C1–C2	13.7(6)	Cu1–N2–C9–C8	2.7(6)	Cu2–N4–C58–C59	169.7(6)
N1–Cu–N2–C2	4.01(14)	N2–Cu1–N1–C2	2.03(3)	N1–Cu1–N2–C9	−0.5(4)	Cu2–N3–C57–C58	0.1(7)

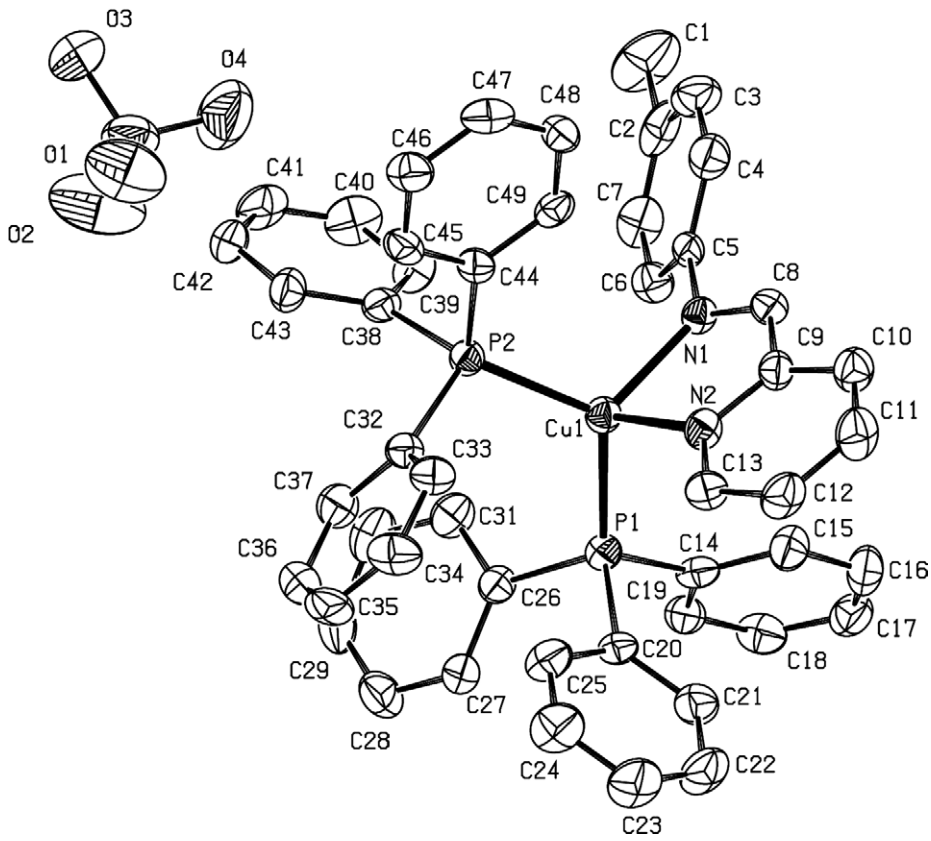

Fig. 4. ORTEP view of the crystal structure of $[Cu(A)(PPh_3)_2]ClO_4$ (**2a**) showing the atom labelling scheme. The thermal ellipsoids enclose 50% of the electronic density. Solvent molecules and hydrogen atoms are omitted for clarity.

up due to the steric effects from the bulky Ph_3P ligands. The average Cu–N and Cu–P bond distances are 2.098 and 2.251 Å, respectively, and are comparable to those reported for $[Cu(dmp)(PPh_3)_2]NO_3$ (2.117(6) and 2.294(2) Å) [29,40].

The chelate ring in complex **2a** is also nearly planar (Table 4) with some strain caused by the deviation from 120° angle about the N-atom (Cu1–N1–C5 126.1(3)°; Cu1–N2–C13 129.7(4)° in I; Cu2–N3–C54 128.7(4)°; Cu2–N4–C62 131.1(6)° in II). The dihedral angle between the chelate ring (Cu–N–C–C–N) and the plane defined by P1–Cu1–P2 is 75(1)° (and 73(1)° in the other molecule of the asymmetric unit) and agrees well with the 82.2° value for $[Cu(dmp)(PPh_3)_2]NO_3$ [25,36].

3.3. Electrochemistry

The electrochemical behavior of the complexes was examined by means of cyclic voltammetry in CH_2Cl_2. The four ligands are electroinactive in the working potential region. The complexes show a quasireversible $Cu^{II/I}$ couple (Table 2) and the ratio of the anodic and cathodic peak currents (i_{pa}/i_{pc}), approaches 1 as the scan rate increases. The peak-to-peak separations increase as the scan rate is changed from 50 mV/s to 500 mV/s.

The $Cu^{II/I}$ potential in a $Cu^{I}N_4$ chromophore is believed to increase with increasing π-acidity of the ligands and the resistance to tetrahedral distortion occurring in the corresponding $Cu^{II}N_4$ chromophore [20,41]. Although, a higher degree of conjugation exists in **1a**–**1d** relative to **2a**–**2d**, the existence of bulkier ligands in **2a**–**2d** which prevent the inner-sphere reorganization to a flattened tetrahedral, more appropriate to Cu(II) oxidation state, play a key role in shifting the oxidation potential to higher values for complexes **2a**–**2d** relative to **1a**–**1d**. However, the potential is approximately insensitive to the methyl substituents on the phenyl ring of ligands in the complexes **1a**–**1d** and/or **2a**–**2d**.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structures **1b**, **1c** and **2a** reported in this paper have been deposited with the Cambridge Crystallographic Data Center, no. CCDC 612098–612100, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/conts/retrieving.html). Supplementary data

associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.08.011.

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