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FULL PAPER

First Schiff base of vinylamine and an α-diketone: a novel N,N donor ligand with extensive conjugation. Synthesis, properties and its copper(I) complexes †

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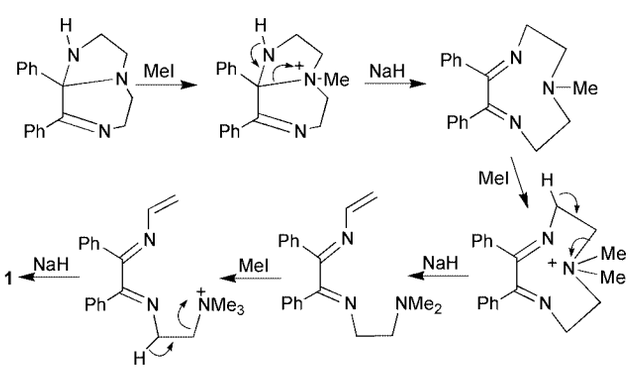
Exhaustive methylation of 8,8a-diphenyl-1,2,3,5,6,8a-hexahydroimidazo[1,2-*a*]pyrazine by NaH and CH_3I in dehydrated tetrahydrofuran yielded 4,5-diphenyl-3,6-diazaocta-1,3,5,7-tetraene (**1**). Using **1** as an N,N donor ligand, cationic copper(I) complexes of the type $[Cu(\mathbf{1})_2]X{\cdot}nH_2O$ ($X^- = ClO_4^-$, $n = 1.5$; $X^- = PF_6^-$, $n = 0$) and $[Cu(\mathbf{1})(PPh_3)_2]X$ ($X^- = ClO_4^-$ or PF_6^-) have been synthesized. Compound **1** and its copper(I) complexes have been thoroughly characterised by ^1H NMR (300 MHz). The $Cu^{II/I}$ potential in $[Cu(\mathbf{1})_2]X{\cdot}nH_2O$ is rather high, 0.92 V *vs.* SCE in CH_2Cl_2 at a glassy carbon electrode. This indicates that **1** is a potential π acid which preferentially stabilises copper(I) much more than copper(II). It is photoluminescent in fluid solution, its emission being somewhat quenched in $[Cu(\mathbf{1})_2]X{\cdot}nH_2O$.

A few Schiff bases of vinylamines are known.[1,2] Since vinylamine is not readily available,[3] these have been obtained circuitously, mainly by thermolysis (dehydrogenation or dehydrohalogenation) of appropriate precursors.[1,2] Moreover, the known Schiff bases of vinylamine can in principle be synthesized by condensing it with appropriate monoketones. So far, no Schiff base of vinylamine is known which can be derived from an α-diketone. However such Schiff bases are envisaged to be very important from the co-ordination chemistry point of view as these can provide novel bidentate N-donor ligands with extensive conjugation. Herein we report the synthesis and properties of the first example, 4,5-diphenyl-3,6-diazaocta-1,3,5,7-tetraene **1**, which in principle can be obtained by 1+2 condensation of benzil and vinylamine.

Results and discussion

The novel Schiff base **1** has been obtained as a hemihydrate during our attempt to methylate 8,8a-diphenyl-1,2,3,5,6,8a-hexahydroimidazo[1,2-*a*]pyrazine (DPHP) with sodium hydride and methyl iodide. A tentative mechanism for the reaction is proposed in Scheme 1. The reaction can be described as exhaustive methylation of DPHP. In this mechanism, the bridge-head N is proposed to be methylated first yielding a hitherto unknown triaza macrocycle 7-methyl-2,3-diphenyl 1,4,7-triazanona-1,3-diene. Subsequently this N atom is proposed to undergo further methylation and finally leaves as trimethylamine resulting in **1**.



Scheme 1 A proposed reaction mechanism.

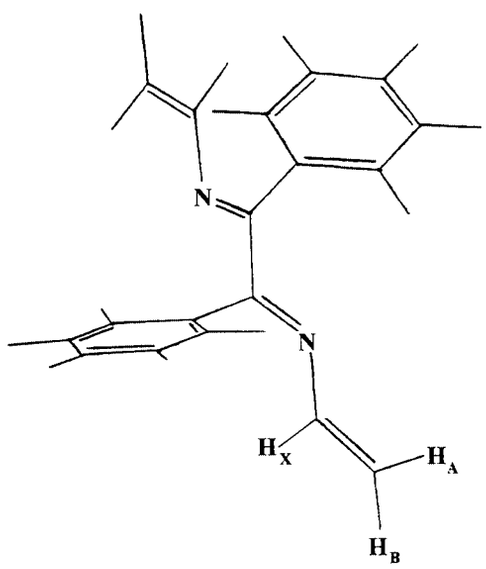


Fig. 1 A line drawing of the stereo view of the minimum energy gas phase structure of compound **1** as obtained by AM1 calculations together with the labelling scheme for the vinyl protons.

The minimum energy gas phase structure of **1** as obtained by AM1 calculations[4] (using MOPAC, version 1.10) is described in Fig. 1. The dihedral angle N=C–C=N is calculated as 98° (O=C–C=O dihedral angle in benzil in the solid state[5] is 70°). The lone pairs on the two imino N atoms in Fig. 1 are *syn* to each other. The other two possible geometric isomers, where the nitrogen lone pairs can be in *anti-anti* or in *syn-anti* orientations, are slightly higher in energy. The ^1H NMR spectrum of $\mathbf{1}{\cdot}0.5H_2O$ in $CDCl_3$ (supplementary material) shows that the C_2 axis of symmetry predicted theoretically for **1** in the gas phase

† Supplementary data available: 300 MHz ^1H NMR spectrum of $\mathbf{1}{\cdot}0.5H_2O$ in $CDCl_3$ available from BLDSC (SUPP. NO. 57702, 2 pp.). See Instructions for Authors, Issue 1 (http://www.rsc.org/dalton).

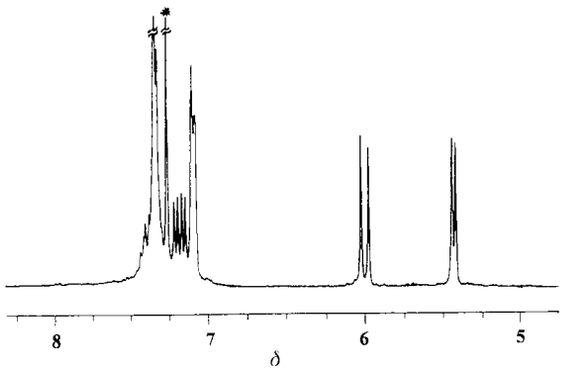


Fig. 2 300 MHz ^{1}H NMR spectrum of $[Cu(\mathbf{1})_2]ClO_4\cdot 1.5H_2O$ in $CDCl_3$ (reference: TMS) in the region δ 5–8. The peak marked by an asterisk is due to the solvent. For the assignments of the other peaks, see Experimental section.

(Fig. 1) prevails at least in solution. The phenyl protons resonate in the region δ 7.82–7.78 and 7.43–7.37. The double doublet around δ 6.87 is assigned to H_X, the doublet around δ 5.68 with higher J value to the proton *trans* to H_X, *i.e.* H_A, and the doublet around δ 5.14 with lower J value to the proton *cis* to H_X, *i.e.* H_B; $J_{AX} = 14.4$ and $J_{BX} = 7.2$ Hz; J_{AB} is not observed. The assignments of the vinyl protons in **1** have been made in keeping with those in other vinyl compounds.[6]

In the IR spectrum, compound **1** shows a very strong and sharp band at 1550 cm^{-1} with no band appearing at an energy above it up to 2940 cm^{-1}. This we assign as ν(C=N). The occurrence of the C=N stretching frequency at such a low energy is due to the conjugation present in **1**. This conjugation suggests that **1** is a potential π acid that can bind a transition metal ion through the N atoms and stabilise lower oxidation state(s) of the metal. Accordingly we wanted to synthesize air stable copper(I) complexes of **1** in the first instance. Reaction of $[Cu(CH_3CN)_4]X$ ($X^- = ClO_4^-$ or PF_6^-) with **1** in 1:2 molar proportion in dehydrated methanol under a dry N_2 atmosphere yields homoleptic copper(I) complexes of formulation $[Cu(\mathbf{1})_2]X\cdot nH_2O$ ($X^- = ClO_4^-$, $n = 1.5$; $X^- = PF_6^-$, $n = 0$) which are bluish black in the solid state. Many copper(I) complexes can be prepared by treating a copper(II) salt with a ligand in appropriate proportion in dehydrated alcohol in the presence of the reducing agent hydrazine hydrate, see ref. 7 for an example. Such a synthetic approach has been found to be ineffective in our case. Our homoleptic copper(I) complexes are quite stable towards aerial oxidation, for at least seven days in the solid state, about 3 h in methanol and about 6 h in dichloromethane. If a solution of $[Cu(\mathbf{1})_2]X\cdot nH_2O$ is allowed to stand in air, slowly the intensity of the blue colour decreases to a faint blue. That the ligand moiety remains intact in $[Cu(\mathbf{1})_2]X\cdot nH_2O$ is evident from the ^{1}H NMR spectrum (see Experimental section and Fig. 2); the vinyl protons of free **1** are uniformly shifted downfield by *ca.* 0.3 ppm on binding Cu^I with the J values remaining more or less unchanged. The bis complexes of copper(I), $[Cu(\mathbf{1})_2]X\cdot nH_2O$, show an intense MLCT band in solution around 615 nm giving rise to a deep blue colour. The rather low energy of this band indicates the presence of an accessible low-lying π* orbital in **1** which arises because of the extensive conjugation possible in **1** in the chelated mode.

In order to assess whether compound **1** is a stronger π acid than PPh_3, we treated $[Cu(\mathbf{1})_2]X\cdot nH_2O$ with the phosphine in 1:2 molar proportion in dehydrated methanol under a N_2 atmosphere. It is found that PPh_3 displaces **1** to give rise to $[Cu(\mathbf{1})(PPh_3)_2]X$ ($X^- = ClO_4^-$ or PF_6^-) in *ca.* 30% yield [reaction (1)]. Subsequently we found that the yield of phosphine

$$[Cu(\mathbf{1})_2]X\cdot nH_2O + 2\ PPh_3 \longrightarrow [Cu(\mathbf{1})(PPh_3)_2]X + \mathbf{1} + n\ H_2O \quad (1)$$

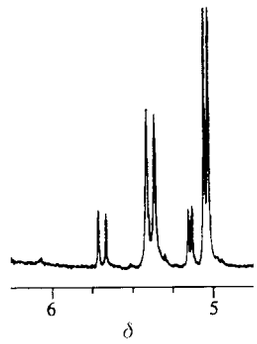


Fig. 3 300 MHz spectrum of $[Cu(\mathbf{1})(PPh_3)_2]ClO_4$ in $CDCl_3$ (reference: TMS) in the region δ 5–6. For the assignments of the peaks and the J values, see Results and discussion.

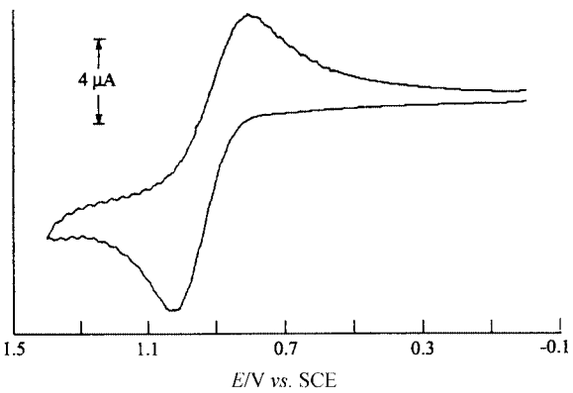


Fig. 4 Cyclic voltammogram (scan rate = 50 mV s^{-1}) of $[Cu(\mathbf{1})_2]PF_6$ in CH_2Cl_2 (0.1 mol dm^{-3} Bu_4NClO_4) at a planar glassy carbon electrode.

complexes $[Cu(\mathbf{1})(PPh_3)_2]X$ increases to *ca.* 50% when $[Cu(CH_3CN)_4]X$, **1** and PPh_3 are allowed to react directly in 1:1:2 stoichiometry in dehydrated methanol under a dry N_2 atmosphere. It is really interesting that these two phosphine complexes are completely devoid of the 615 nm band. However, they do not obey Beer's law. This can be understood from their NMR spectra (Fig. 3) which show that in a solution of $[Cu(\mathbf{1})(PPh_3)_2]X$ the ligand partially dissociates from the metal [eqn. (2)]. The NMR spectra of the complexes

$$[Cu(\mathbf{1})(PPh_3)_2]^+ \rightleftharpoons [Cu(PPh_3)_2]^+ + \mathbf{1} \quad (2)$$

$[Cu(\mathbf{1})(PPh_3)_2]ClO_4$ and $[Cu(\mathbf{1})(PPh_3)_2]PF_6$ are identical with the phenyl protons and the H_X protons resonating in the region δ 7.96–6.75. Doublets observed (Fig. 3) at δ 5.68 ($J = 14.4$) and 5.14 ($J = 7.0$ Hz) are assigned respectively to the H_A and H_B protons of free **1**. The doublets (Fig. 3) at δ 5.39 ($J = 15.0$) and 5.04 ($J = 7.5$ Hz) are respectively assigned to the H_A and H_B protons of **1** in the chelated mode. Existence of the species $[Cu(PPh_3)_2]^+$, invoked in eqn. (2), is known in the solid state.[8]

The electrochemical behaviour of the complexes $[Cu(\mathbf{1})_2]ClO_4\cdot 1.5H_2O$ and $[Cu(\mathbf{1})_2]PF_6$ has been examined by cyclic voltammetry in dichloromethane at a glassy carbon electrode. Identical voltammograms are obtained for the two complexes (Fig. 4). These show a quasireversible $Cu^{II/I}$ couple with an $E_{\frac{1}{2}}$ of 0.92 V *vs.* SCE (saturated calomel electrode). The peak-to-peak separation for this couple in cyclic voltammetry varies from 210 to 635 mV as the scan rate is changed from 10 mV s^{-1} to 1 V s^{-1}. The high potential of the $Cu^{II/I}$ couple in $[Cu(\mathbf{1})_2]X\cdot nH_2O$ shows that our ligand **1** is capable of stabilising Cu^I much more than Cu^{II}. For a ready appraisal of the magnitude of the potential, we mention that this couple in $[Cu(bipy)_2]^+$ has a potential of *ca.* 0.01 V *vs.* SCE in 50% 1,4-dioxane–water.[9] The highest potential for the $Cu^{II/I}$ couple in a Cu^IN_4 chromophore reported

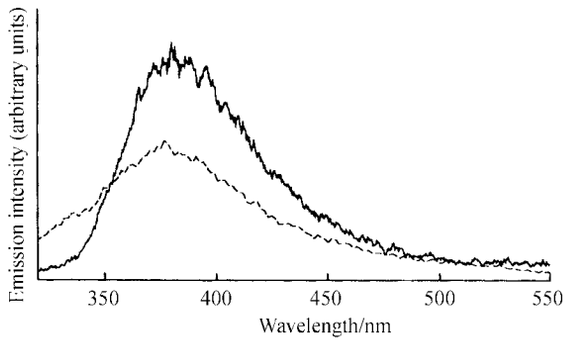


Fig. 5 Emission spectra of compound **1**·0.5H_2O (——) and [Cu(**1**)$_2$]ClO_4·1.5H_2O (– – – –) in methanol at room temperature on excitation at 290 nm. The absorbance at 290 nm in both cases is 0.04.

so far is 1.55 V *vs.* SCE.[10] It is now believed that the $Cu^{II/I}$ potential in a $Cu^{I}N_4$ chromophore increases with the π acidity of the ligand and the extent of tetrahedral distortion in the corresponding $Cu^{II}N_4$ chromophore.[9–12] Both the factors may be operative in our case. Incidentally, so far, we have not been able to isolate any homoleptic copper(II) complex of **1**. Upon treating $Cu(ClO_4)_2$·6H_2O with **1** in 1:2 molar proportion in dehydrated methanol, initially a light green colour develops which changes to a faint blue on standing; from the reaction mixture, finally only the ligand can be recovered.

The Schiff base **1** shows a broad, featureless, intense band at 275 nm in its absorption spectrum in methanol. Upon excitation at 290 nm (within the envelope of the 275 nm band) at room temperature in methanol it gives rise to a weak emission band with the maximum at 370 nm (Fig. 5). The emission quantum yield (φ) is determined to be 8.2×10^{-3} with reference to 2-methylindole.[13] This emission is somewhat quenched in the copper(I) complex [Cu(**1**)$_2$]ClO_4·1.5H_2O in methanol ($\lambda_{excitation}$, 290 nm; $\lambda_{emission}$, 370 nm; Fig. 5; φ, 3.3×10^{-3}). The change of anion from perchlorate to hexafluorophosphate has negligible effect on φ ([Cu(**1**)$_2$]PF_6 in methanol: $\lambda_{excitation}$, 290 nm; $\lambda_{emission}$, 370 nm; φ, 3.4×10^{-3}). Quenching of the fluorescence of an organic fluorophore by a transition metal is a very common phenomenon; only in some rare cases, transition metals can induce enhancement of the fluorescence of an organic fluorophore.[14]

Concluding remarks

Here we have shown that methylation of 8,8a-diphenyl-1,2,3,5,6,8a-hexahydroimidazo[1,2-*a*]pyrazine yields a new N,N donor ligand **1** which can be regarded as a 1+2 Schiff base of benzil and vinylamine. Considering the procedures used by others to generate molecules which can be called 1 + 1 Schiff bases of vinylamine and appropriate mono ketones,[1,2] we feel that given the molecule **1** it will not be very easy to devise a suitable synthetic route. However, a few 1 + 2 Schiff bases of 2,6-diacetylpyridine and some primary amines containing olefinic groups are known.[15] Here we have also demonstrated by synthesising its bis copper(I) complexes with a rather high potential $Cu^{II/I}$ couple that **1** is a potential π acid and capable of stabilising lower oxidation states of a transition metal. This π acidity arises because of the extensive conjugation present in **1**. In order to determine the π-acid strength of **1** electrochemically (to be precise, in terms of Chatt's ligand constant[16] and Lever's ligand constant[17]), we are at present engaged in developing its ruthenium(II) chemistry.

Experimental

General

The complexes [Cu(CH_3CN)$_4$]ClO_4 and [Cu(CH_3CN)$_4$]PF_6 were synthesized by reported procedures.[18,19] All other reagents were procured commercially. Copper was estimated gravimetrically as CuSCN. Microanalyses were performed by a Perkin-Elmer 2400II elemental analyser. Molar conductance was determined by a Systronics (India) direct reading conductivity meter (model 304). The melting point of **1**·0.5H_2O was determined by an apparatus from CBC Power System (Calcutta, India) and is uncorrected. IR spectra (KBr disc) were recorded on a Perkin-Elmer 783 spectrophotometer, UV–VIS spectra on a Shimadzu UV-160A spectrophotometer, ^{1}H NMR spectra (in $CDCl_3$) by a Brucker DPX300 spectrometer and EI (electron impact) mass spectra on a Finnigan-Mat 1020 instrument. All the photoluminescnce studies were performed in air using a Hitachi F-4500 spectrofluorimeter. Cyclic voltammetry was performed at a planar EG&G PARC G0229 glassy carbon milli electrode using an EG&G PARC electrochemical analysis system (model 250/5/0) in purified and anhydrous dichloromethane under a dry nitrogen atmosphere in conventional three electrode configurations. Under the experimental conditions employed here, the ferrocene–ferrocenium couple appears at 0.468 V *vs.* SCE with a peak-to-peak separation of 114 mV at a scan rate of 50 mV s^{-1}.

Syntheses

4,5-Diphenyl-3,6-diazaocta-1,3,5,7-tetraene hemihydrate (1·0.5H_2O). To a 25 ml solution of 0.56 g (2 mmol) of DPHP, synthesized by a previously published procedure,[20] in dehydrated tetrahydrofuran was added 0.072 g (3 mmol) of NaH and stirred for 3 h. Then the mixture was cooled to 0 °C and 0.4 ml of CH_3I (6 mmol) was added and stirred for 12 h at 0 °C. After two hours' of stirring, another 0.4 ml of CH_3I was added. Then the reaction mixture was warmed to room temperature and filtered. Solvent was removed completely from the filtrate at room temperature under reduced pressure to obtain a yellow mass. It was extracted with 50 ml of diethyl ether. The light yellow ether layer was washed thoroughly thrice with 100 ml of water and then dehydrated by adding anhydrous sodium sulfate. Complete removal of ether yielded **1**·0.5H_2O as a pale yellow solid. It was recrystallised from *n*-hexane and stored in the dark. Yield 0.30 g (55%) mp 100–104 °C (Found: C, 80.34; H, 6.34; N, 10.34. $C_{18}H_{17}N_2O_{0.5}$ requires C, 80.26; H, 6.37; N, 10.40%). EI MS: *m*/*z* 260 (**1**$^+$, 42%). IR/cm^{-1} (KBr): 1550vs (C=N). δ_H (300 MHz, $CDCl_3$, TMS) 7.82–7.78 (m, 4 H, phenyl), 7.43–7.37 (m, 6 H, phenyl), 6.91–6.83 (dd, 2 H, J = 7.2 and 14.4, H_X), 5.68 (d, 2 H, J = 14.4, H_A), 5.14 (d, 2 H, J = 7.2 Hz, H_B) and 1.64 (br, H_2O). UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): (CH_3OH) 275 (32 300) and 222 (24 800).

[Cu(1)$_2$]ClO_4·1.5H_2O. To a solution of 0.26 g (1 mmol) of compound **1**·0.5H_2O in 20 ml of dehydrated methanol, 0.165 g (0.5 mmol) of solid [Cu(CH_3CN)$_4$]ClO_4 was added and stirred for 6 h under a dry N_2 atmosphere. (Within 5 min of stirring, the yellow solution became blue.) Then the reaction mixture was added to 200 ml of diethyl ether dropwise with constant stirring. Shining dark microneedles started separating. The mixture was kept in a refrigerator for 30 min. Then the bluish black compound was filtered off, washed with 10 ml of diethyl ether, dried *in vacuo* over fused $CaCl_2$ and stored in vacuum. Yield 0.075 g (20%) (Found: C, 60.81; H, 4.89; Cu, 8.91; N, 7.89. $C_{36}H_{35}ClCuN_4O_{5.5}Cl$ requires C, 60.81; H, 4.97; Cu, 8.94; N, 7.88%). IR/cm^{-1} (KBr): 1600br (C=N) and 1090vs (br) (ClO_4). Λ_M (CH_3OH): 90 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). δ_H (300 MHz, $CDCl_3$, TMS) 7.38–7.32 (m, 6 H, phenyl), 7.10–7.08 (m, 4 H, phenyl), 7.22–7.15 (dd, 2 H, J = 7.1 and 14.4, H_X), 5.99 (d, 2 H, J = 14.4, H_A), 5.43 (d, 2 H, J = 7.1 Hz, H_B) and 1.63 (br, H_2O). UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): (CH_3OH) 615 (6500), 427 (2000), 293 (23 200) and 214 (39 600); (Nujol mull) 630, 435, 370 and 265 nm.

[Cu(1)$_2$]PF_6. This was synthesized by a procedure similar to that described for [Cu(**1**)$_2$]ClO_4·1.5H_2O by starting with 0.5

mmol $[Cu(CH_3CN)_4]PF_6$. Yield 0.145 g (40%) (Found: C, 59.21; H, 4.40; Cu, 8.67; N, 7.71. $C_{36}H_{32}CuF_6N_4P$ requires C, 59.28; H, 4.42; Cu, 8.72; N, 7.68%). IR/cm^{-1} (KBr): 1600br (C=N), 830vs (br) (PF_6). Λ_M (CH_3OH): 95 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). δ_H (300 MHz, $CDCl_3$, TMS) 7.39–7.32 (m, 6 H, phenyl), 7.08–7.06 (m, 4 H, phenyl), 7.22–7.15 (dd, 2 H, J = 7.1 and 14.4, H_X), 5.99 (d, 2 H, J = 14.4, H_A) and 5.44 (d, 2 H, J = 7.1 Hz, H_B). UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): (CH_3-OH) 618 (7500), 426 (2000), 279 (28 000) and 208 (45 700); (Nujol mull) 635, 430, 360 and 265 nm.

$[Cu(1)(PPh_3)_2]ClO_4$. To a solution of 0.26 g (1 mmol) of compound **1**·$0.5H_2O$ in 20 ml of dehydrated methanol, 0.165 g (0.5 mmol) of solid $[Cu(CH_3CN)_4]ClO_4$ was added and stirred under a dry N_2 atmosphere. Within 5 min of stirring the yellow solution became blue. After stirring for 1 h, 0.26 g (1 mmol) of solid PPh_3 was added and the reaction stirred for 2 h maintaining the N_2 atmosphere. (Within 2 min of the addition of PPh_3, the blue mixture became reddish.) Then the solvent was evaporated under reduced pressure at 50 °C. The reddish yellow residue was triturated with diethyl ether to obtain a light yellow solid. It was filtered off, washed with diethyl ether, dried *in vacuo* over fused $CaCl_2$ then recrystallised from dichloromethane–hexane (65–70 °C fraction from light petroleum). Yield 0.26 g (≈55%) (Found: C, 68.36; H, 5.00; Cu, 6.62; N, 2.91. $C_{54}H_{46}ClCu\,N_2O_4P_2$ requires C, 68.40; H, 4.90; Cu, 6.70; N, 2.95%). IR/cm^{-1} (KBr): 1580br (C=N) and 1080vs (br) (ClO_4). Λ_M (CH_3OH): 101 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). δ_H (300 MHz, $CDCl_3$, TMS): 7.96–6.75 (phenyl protons + the H_X protons); other protons, see Fig. 3 and Results and discussion. UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): (CH_3OH; concentration c, 0.058 mol dm^{-3}) 460 (1350), 268 (31 000) and 214 (55 400); (Nujol mull) 470 and 270 nm.

$[Cu(1)(PPh_3)_2]PF_6$. This was synthesized by a procedure similar to that given for $[Cu(\mathbf{1})(PPh_3)_2]ClO_4$ by starting with 0.5 mmol $[Cu(CH_3CN)_4]PF_6$. Yield 0.25 g (≈50%) (Found: C, 65.30; H, 4.69; Cu, 6.45; N, 2.78. $C_{54}H_{46}CuF_6N_2P_3$ requires C, 65.27; H, 4.67; Cu, 6.40; N, 2.82%). IR/cm^{-1} (KBr): 1590br (C=N) and 830vs (br) (PF_6). Λ_M (CH_3OH): 102 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). δ_H (300 MHz, $CDCl_3$, TMS): 7.96–6.75 (phenyl protons + the H_X protons); other protons, see Fig. 3 and Results and discussion. UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): (CH_3OH; c, 0.056 mol dm^{-3}) 460 (1200), 268 (32 600) and 216 (60 750); (Nujol mull) 475 and 270 nm.

CAUTION: Though while working with the perchlorate compounds described here we have not met with any incident, care should be taken in handling them as perchlorates are potentially explosive. These should not be prepared and stored in large amounts.

Acknowledgements

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