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Synthesis and mesomorphic properties of novel phenacylpyridines and their copper(II) complexes

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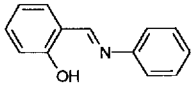
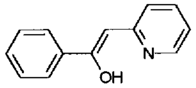
The synthesis, characterization and liquid crystal properties of a homologous series of a new class of alkoxyphenacylpyridine ligands and their copper(II) complexes are reported. According to textural observations and calorimetric data, ligands with $n = m \geqslant 8$ and copper complexes with $n = m \geqslant 6$, where n, m denote the number of carbon atoms in the alkoxy chains, exhibit liquid crystal properties. The mesogenic ligands display monotropic nematic phases, while the mesogenic copper(II) complexes give enantiotropic smectic A phases.

1. Introduction

In recent years metal complexes with liquid crystal properties, metallomesogens, have attracted considerable attention since they offer new properties in liquid crystal materials arising from metal coordination—new shapes, colour and paramagnetism [1]. An increasing number of ligands has been found to form liquid crystals by incorporating metal atoms [1, 2]. However, the influence of the metals on the mesophase and structure–property relationships for metallomesogens are still not clear. Our interest and effort have been directed towards understanding these aspects. Traditionally, useful ligands in the study of these correlations are provided by Schiff's bases **I** derived from salicylaldehide. A number of bischelates of Schiff's bases have been studied and some correlations between structure and mesomorphic properties have been established [1–6].



I



II

In the course of our study of organometallic complexes with chiral Schiff's bases prepared by reacting phenacylpyridines **II** with chiral amines [7], we noticed the high chemical and thermal stability and complete enolization of the latter. Phenacylpyridine **II** is isostructural with Schiff's base **I**. The azomethine sub-unit in the compounds **II** is incorporated into the stable heteroaromatic ring, whereas the acidity of the enolic hydroxy group matches that of the phenolic group in **I**. Easy availability of **II** from substituted benzoic esters and 2-picoline prompted us to use this reaction with 4-alkoxybenzoic esters and 5-alkoxy-2-methylpyridines. In this work we present the synthesis and liquid crystalline properties of a homologous series of phenacylpyridine ligands, derivatives of **II**, and their copper(II) complexes.

2. *Synthesis and characterization*

The synthesis of the ligands and corresponding copper(II) complexes is illustrated in the scheme.

The methyl 4-alkoxybenzoates **3a–f** were prepared in 70–90 per cent yield from methyl 4-hydroxy-benzoate **2** and the alkyl bromide in acetone using potassium carbonate as base [8]. A series of 5-alkoxy-2-methylpyridines **5 a–f** was prepared in the same way, starting from 5-hydroxy-2-methylpyridine **4** and the alkyl bromide, in 60–80 per cent yield.

The key step in the synthesis of 2-phenacylpyridines is acylation of the carbanion of the 5-alkoxy-2-methylpyridine with an appropriate ester after regioselective metallation of the methyl group. Metallation of picoline isomers with phenyl lithium, lithium di-isopropylamide in tetrahydrofuran (LDA–THF), and lithium bistrimethylsilylamide have been examined. Using phenyl lithium [9, 10] or LDA–THF [7, 11] as metallating agent for the acylation of 2-methyl-5-octyloxypyridine **5 d** with ethyl benzoate, a complex mixture was regularly isolated. It consisted of product **8**, obtained in *c.* 11 per cent yield, compounds **9** and **10** in *c.* 10 per cent yield, and benzophenone as the side product of nucleophilic attack of phenyllithium on ethyl benzoate. The structures of **9** and **10**, as determined by NMR spectroscopy, reveal carbanion generation also at positions 2- and 4- of the pyridine ring. Thus, metallation of 2-methyl-5-octyloxypyridine, followed by the addi-

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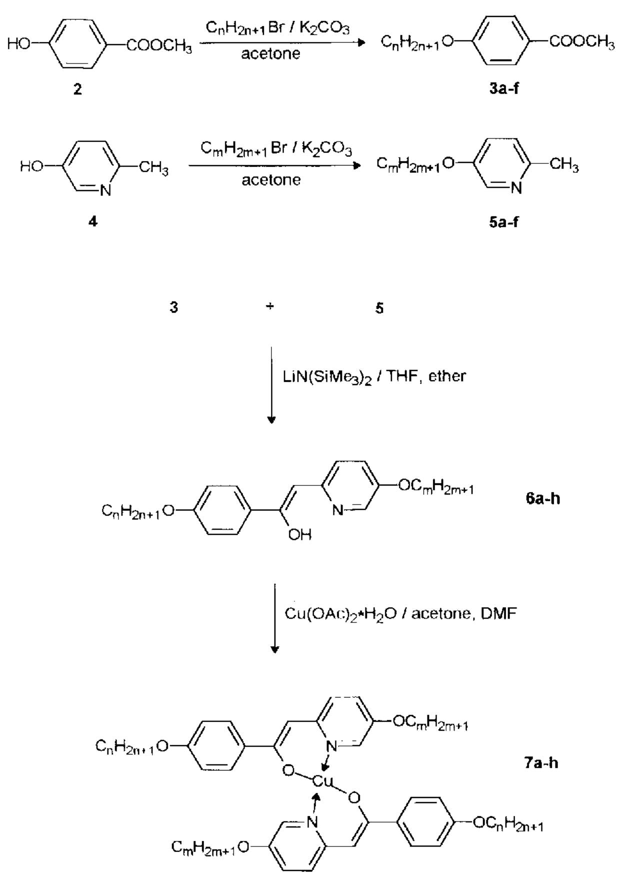
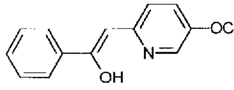
*Author for correspondence.



	a	b	c	d	e	f	g	h
n	2	4	6	8	11	13	8	13
m	2	4	6	8	11	13	2	2

Scheme.

tion of ethyl benzoate did not furnish the desired product in satisfactory yields.



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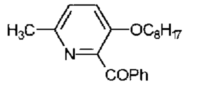

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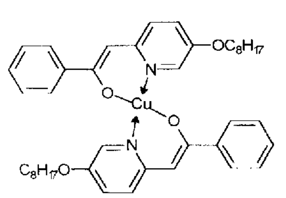

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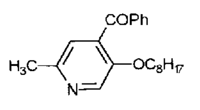

10

Lithium bis-trimethylsilylamide, used as a 1 M solution in THF, gave promising results. It had already been used, along with some other hindered lithium silyl bases, for regiospecific generation of the enolate anion of methyl ketones [12]. Acylation of 2-methyl-5-octyloxypyridine **5d** with ethyl benzoate afforded 37 per cent of **8**; the yield was somewhat lower (20–25 per cent) with methyl 4-octyloxybenzoate. Metallation at room temperature for 3 h using the molar ratio 2:2:1 of base:picoline:ester increased the yields up to 60 per cent. Crude products **6a–h** have been purified by column chromatography on silica gel with toluene/ether as eluent.

Copper(II) complexes **7a–h** have been prepared from the appropriate free ligand and copper(II) acetate monohydrate in the solvent mixture acetone/DMF; with some of the ligands, a small amount of toluene was added to improve their solubility.

The solid state IR spectra of the ligands showed a characteristic broad band between 3300–3600 cm^{-1} (O–H stretch), a doublet at 1615 cm^{-1} (C=C stretch) and a multiplet at 1250 cm^{-1} (C–O stretch). The presence of O–H and C=C vibrations reveals that the enolic form of the ligands exists in the solid state. In solution, they undergo keto–enol tautomerism and, according to their ^{1}H NMR spectra in chloroform solution, they are mainly present in the keto form (>98 per cent). Table 1 summarizes yields and NMR data for the phenacylpyridines **6a–h**.

The ν(O–H) band is absent in the infrared spectra of the copper(II) complexes. This indicates that the alcoholic proton is exchanged upon complexation. The ν(C=C) band of the free ligands is shifted by 25 cm^{-1} to a lower wave number (1590 cm^{-1}), suggesting that the copper ion is coordinated to the enolic oxygen and pyridine nitrogen.

The UV–Vis spectra of the ligands in cyclohexane solution are characterized by two broad absorption bands with the maxima between 272 and 284 nm, depending on the ligand, for the first band, and at 359 nm for the second band. Upon complexation with copper(II) acetate, the long wavelength band shifts to 396 nm and the molar extinction coefficient increases 3–6 times compared with the ligands. These results confirm coordination of the ligand to copper(II) ion.

Elemental analysis confirmed the proposed structures for all the newly prepared compounds. Tabulated data have been deposited with the British Library, Lending Division, by quoting SUP 16530 according to the procedure described at the end of this issue.

3. Results and discussion

The mesomorphic behaviour of all the compounds prepared was studied by polarizing optical microscopy and the associated enthalpy changes were determined by differential scanning calorimetry (DSC). Tables 2 and 3, respectively, summarize the mesomorphic transition temperatures and enthalpies for the homologous series of free ligands and copper complexes with $n = m$, where

Table 1. Yields and NMR data for the compounds **6a–h**.

Compound	Yield/per cent	^{1}H NMR ($CDCl_3$/TMS), *δ*/ppm, *J*/Hz	^{13}C NMR ($CDCl_3$/TMS), *δ*/ppm
6a	39	1·39–1·45 (m, 6 H), 4·01–4·12 (m, 4 H), 4·37 (s, 2 H), 6·89 (d, 2 H, *J*=6), 7·15–7·23 (m, 2 H), 8·03 (d, 2 H, *J*=6), 8·23 (d, 1 H, *J*=2·7)	14·4, 14·5, 47·1, 63·6, 63·8, 114·1, 121·8, 124·2, 129·4, 131·1, 137·3, 147·3, 153·8, 163·0, 195·9
6b	65	0·94–0·99 (m, 6 H), 1·45–1·52 (m, 4 H), 1·72–1·80 (m, 4 H), 3·95–4·03 (m, 4 H), 4·37 (s, 2 H), 6·89 (d, 2 H, *J*=6), 7·12–7·23 (m, 2 H), 8·03 (d, 2 H, *J*=6), 8·23 (d, 1 H, *J*=2·7)	13·5, 18·9, 30·9, 31·0, 31·1, 47·2, 67·8, 67·9, 114·1, 121·8, 124·2, 129·4, 131·1, 137·3, 147·2, 154·0, 163·2, 195·9
6c	51	0·88–1·81 (m, 22 H), 3·94–4·02 (m, 4 H), 4·37 (s, 2 H), 6·90 (d, 2 H, *J*=6), 7·12–7·22 (m, 2 H), 8·03 (d, 2 H, *J*=6), 8·22 (d, 1 H, *J*=2·7)	13·9, 22·4, 25·5, 28·9, 29·0, 31·4, 47·2, 68·1, 68·3, 114·0, 121·7, 124·1, 129·2, 131·0, 137·2, 147·1, 153·8, 163·0, 195·7
6d	26	0·88–1·78 (m, 30 H), 3·89–4·06 (m, 4 H), 4·37 (s, 2 H), 6·89 (d, 2 H, *J*=6), 7·14–7·18 (m, 2 H), 8·02 (d, 2 H, *J*=6), 8·16 (d, 1 H, *J*=2·7)	13·9, 22·5, 25·8, 29·0, 29·2, 31·6, 47·2, 68·1, 68·3, 114·0, 121·7, 124·0, 129·3, 130·9, 137·2, 147·1, 153·9, 163·1, 195·6
6e	38	0·87–1·81 (m, 42 H), 3·93–4·01 (m, 4 H), 4·37 (s, 2 H), 6·90 (d, 2 H, *J*=6), 7·12–7·22 (m, 2 H), 8·03 (d, 2 H, *J*=6), 8·23 (d, 1 H, *J*=2·7)	13·9, 22·5, 25·8, 28·9, 29·1, 29·2, 29·4, 29·5, 29·8, 29·9, 30·0, 31·7, 47·2, 68·1, 68·3, 114·1, 121·8, 124·1, 129·2, 131·0, 137·2, 147·1, 153·9, 163·1, 195·7
6f	49	0·85–1·76 (m, 50 H), 3·93–4·02 (m, 4 H), 4·37 (s, 2 H), 6·90 (d, 2 H, *J*=6), 7·12–7·22 (m, 2 H), 8·03 (d, 2 H, *J*=6), 8·23 (d, 1 H, *J*=2·7)	14·0, 14·1, 22·7, 22·9, 23·7, 25·9, 26·9, 29·0, 29·1, 29·3, 29·5, 29·6, 30·0, 30·3, 31·9, 47·3, 68·2, 68·4, 114·2, 121·8, 124·2, 129·3, 131·1, 137·3, 147·2, 153·9, 163·2, 195·6
6g	45	0·86–1·81 (m, 18 H), 3·97–4·08 (m, 4 H), 4·37 (s, 2 H), 6·90 (d, 2 H, *J*=6), 7·12–7·23 (m, 2 H), 8·03 (d, 2 H, *J*=6), 8·23 (d, 1 H, *J*=2·7)	14·0, 14·7, 22·6, 25·9, 29·0, 29·2, 29·3, 31·7, 47·3, 63·9, 68·2, 114·2, 121·8, 124·2, 129·3, 131·1, 137·3, 147·3, 153·8, 163·1, 195·7
6h	42	0·86–1·81 (m, 28 H), 3·97–4·08 (m, 4 H), 4·37 (s, 2 H), 6·90 (d, 2 H, *J*=6), 7·12–7·23 (m, 2 H), 8·03 (d, 2 H, *J*=6), 8·23 (d, 1 H, *J*=2·7)	14·1, 14·8, 22·7, 26·0, 29·1, 29·3, 29·7, 31·9, 47·3, 63·9, 68·3, 114·2, 121·9, 124·2, 129·5, 131·1, 137·4, 147·4, 153·8, 163·3, 195·8
8	37	0·86–1·79 (m, 15 H), 3·96 (t, 2 H, *J*=6 Hz), 4·43 (s, 2 H), 7·13–7·22 (m, 2 H), 7·42–7·57 (m, 3 H), 8·04–8·07 (m, 2 H), 8·23 (d, 1 H, *J*=6)	13·9, 22·4, 25·7, 29·0, 29·1, 31·6, 47·3, 68·3, 121·6, 124·1, 124·8, 128·1, 128·4, 128·6, 133·0, 136·3, 137·2, 146·6, 153·9, 197·1

Table 2. Transition temperatures and enthalpies for the phenacylpyridine ligands **6a–f**.

Lignd	*n*	*m*	Transition	T/°C	Δ*H*/kJ mol^{-1}
6a	2	2	Cr–I	118^a	–
6b	4	4	Cr–I	98^a	–
6c	6	6	Cr–I	96^a	–
6d	8	8	Cr–I	83·7	49·5
			I–N	78·0	−11·0
			N–Cr	63·2	−28·6
6e	11	11	Cr–I	90·4	70·8
			I–N	85·6	−15·2
			N–Cr	75·1	−48·0
6f	13	13	Cr–Cr_1	80·4	14·5
			Cr_1–I	95·8	97·1
			I–N	87·9	−22·5
			N–Cr	78·4	−50·4

Cr, crystal; N, nematic; I, isotropic liquid.
[a] Determined by optical microscopy.

Table 3. Transition temperatures and enthalpies for phenacylpyridine copper(II) complexes **7a–f**.

Complex	*n*	*m*	Transition	T/°C	Δ*H*/kJ mol^{-1}
7a	2	2	Cr–I	159^a	–
7b	4	4	Cr–I	152^a	–
7c	6	6	Cr–S_A	145	25·2
			S_A–I	166^a	–
7d	8	8	Cr–Cr_1	106	4·3
			Cr_1–S_A	141	21·5
			S_A–I	161	0·26
7e	11	11	Cr–Cr_1	85	1·7
			Cr_1–S_A	119	18·7
			S_A–I	160	0·5
7f	13	13	C–S_A	110	40·5
			S_A–I	142	1·1

Cr, crystal; S_A, smectic A; I, isotropic liquid.
[a] Determined by optical microscopy.

n,m denote the number of carbon atoms in the alkoxy chains.

All the ligands are thermally stable and their phase transitions were reproducible on subsequent heating. As can be seen in table 2, the first three homologues are non-mesomorphic. Mesomorphism appears from the octyl derivative onwards, homologues **6d–f** showing monotropic nematic transitions. The nematic phase was clearly identified by its very fluid schlieren texture and typical nematic droplets were observed on cooling from the isotropic liquid [13]. The melting points were relatively independent of the chain length.

Cr–I enthalpies as well as enthalpies for the I–N and N–Cr transitions increase with increasing number of carbon atoms in the alkoxy chain. According to DSC only ligand **6f** displays solid state polymorphism.

Copper complexes **7a–f** decompose partially in the isotropic state. The DSC data, see table 3, for these materials were taken at the onset of the signal and correspond to the first heating scan. Comparing with the data reported in table 2 a general trend can be noted; the transition temperatures for the organometallic complexes are significantly higher than those of the parent ligand and decrease as the number of carbon atoms in alkoxy chain increases. The border line for mesomorphic behaviour of the complexes has moved to the lower homologue **7c** ($n = m = 6$), as compared to the free ligand. Similarly to simple copper complexes derived from arylamino Schiff's bases [14], the newly prepared phenacylpyridine complexes display smectic mesomorphism. According to textural observations, complexes **7c–f** show enantiotropic smectic A (S_A) phases characterized by well-defined focal-conic fans interspersed with homeotropic regions. S_A–I enthalpies for the complexes increase with increasing molecular length, but their values are significantly smaller than the isotropization enthalpies for the free ligands. For the complexes **7d** and **7e** solid phase transitions appear on the DSC traces, but they were not observed by optical microscopy. These transitions were not investigated further since we were primarily interested in the mesomorphic transitions.

A plot showing the phase transition temperatures versus the number of carbon atoms in the alkoxy chains for the phenacylpyridine ligands **6a–f** and their copper(II) complexes **7a–f** is given in the figure.

According to these results, the influence of the metal ion is obvious. Contrary to the montropic behaviour of the ligands, the complexes display enantiotropic phase transitions, indicating that metal complexation stabilizes the mesophase. Stabilization of the mesophase by longer alkoxy chains is more pronounced for the complexes than for the ligand series. Finally, incorporation of a metal centre into the molecule of the ligand leads to a more ordered mesophase in the complex. The change is probably caused by differences in molecular geometry between the ligand and the complex, and the greater polarity of the coordination bonds in CuL_2 should enhance transverse intermolecular association, promoting smectic phase formation.

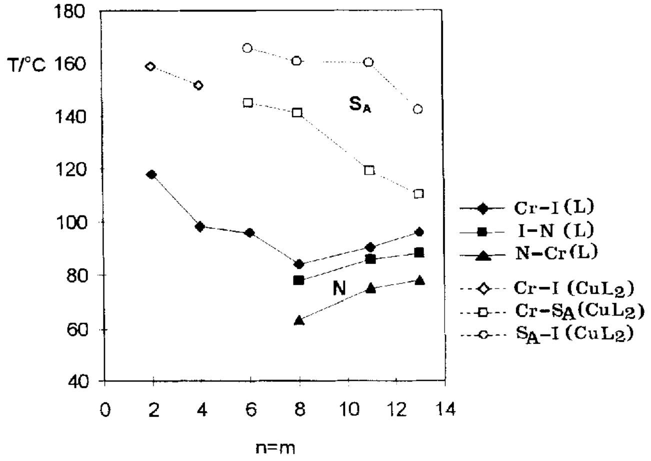

Figure A plot of the phase transition temperatures versus the number of carbon atoms in the alkoxy chain for the phenacylpyridine ligands, L, **6a-f** (solid line) and their copper(II) complexes, CuL_2, **7a-f** (dotted line). For liqand **6f** and complexes **7d**, **7e**, the solid-solid phase transitions are not reported.

The influence of non-symmetric alkoxy chain lengths on the liquid crystalline properties has been examined for the ligands **6g** and **6h** and their copper complexes. The phase transition temperatures and enthalpies are presented in table 4.

The ligand **8** with only one terminal chain is non-mesomorphic, while **6g** and **6h** display very short range, monotropic nematic phases. The enthalpies determined by DSC are given as combined enthalpies, since the mesophase transitions are close in temperature and the peaks are broad. Upon complexation no mesomorphic behaviour appears. This reveals the necessity of two pairs of long alkoxy chains for stabilization of the mesophases of the copper(II) complexes.

4. Experimental

^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions on a JEOL FX 90Q FT spectrometer; shifts are given in ppm downfield from TMS as internal standard. IR spectra were recorded on a Perkin–Elmer 297 spectrophotometer and UV–Vis spectra were recorded on a Phillips PU 8700 UV/Visible spectrophotometer. The optical microscopy observations were made using a Zeiss, Jena polarizing microscope × 150) equipped with hot stage and Oxford Intelligent Temperature Controller ITC 4. The phase transition temperatures were determined using a Perkin–Elmer DSC7 differential

Table 4. Transition tempratures and enthalpies for compounds **6 g**, **6 h**, **8**, **7 g**, **7 h**, **11**.

Compound	*n*	*m*	Transition	T/°C	ΔH/kJ mol^{-1}
6 g	8	2	Cr–I	78·4	39·7
			I–N	53·5	29·9[a]
			N–Cr	47·7	
6 h	13	2	Cr–Cr$_1$	68·3	5·0
			Cr$_1$–I	84·6	60·3
			I–N	61·2	49·7[a]
			N–Cr	54·4	
8	0	8	Cr–I	74[b]	–
7 g	8	2	Cr–I	168[b]	–
7 h	13	2	Cr–Cr$_1$	109	24·5
			Cr$_1$–I	148	55·5
11	0	8	Cr–Crl	111	41·2
			Cr$_1$–I	140	33·1

Cr, crystal; N, nematic; S$_A$, smectic A; I, isotropic liquid.

[a] Low resolution of the peaks-combined enthalpies.

[b] Determined by optical microscopy.

scanning calorimeter (heating and cooling rate: $10^{\circ+}$ min^{-1}).

Compound **2** (see Scheme) was prepared from 4-hydroxybenzoic acid in 82 per cent yield by esterification. 5-Hydroxy-2-methylpyridine **4** was purchased from Aldrich.

4.1. *Preparation of methyl 4-alkoxybenzoates 3 a–f*

A mixture of equimolar quantities (13 mmol) of methyl 4-hydroxybenzoate, alkyl halide and potassium carbonate in acetone (20 ml) was heated under reflux overnight. To the cold reaction mixture water (30 ml) and ether (20 ml) were added. The organic layer was separated and aqueous phase shaken with ether (3 × 20 ml). The combined organic extracts were washed with 2 M NaOH, dried over K_2CO_3 and evaporated *in vacuo*. After purification by distillation or crystallization from a mixture of methanol–water, products **3 a–f** were obtained in 70–90 per cent yield. IR and ^{1}H NMR spectra of the products are consistent with the required formulae.

4.2. *Preparation of 5-alkoxy-2-methylpyridines 5 a–f*

5-Alkoxy-2-methylpyridines were prepared from 5-hydroxy-2-methylpyridine and alkyl halide by a method analogous to that used for **3 a–f**. After distillation, products **5 a–f** were isolated as colourless or slightly yellow oils in 60–80 per cent yield. The structures of the products were confirmed by their IR and ^{1}H NMR spectra.

4.3. *Preparation of phenacylpyridine ligands 6 a–h, 8*

A solution of lithium bis-trimethylsilyamide (4 mmol, 1 M solution in tetrahydrofuran, Aldrich) was added dropwise to the 2-methyl-5-alkoxypyridine (3 mmol) under an argon atmosphere at ambient temperature and stirred for 3 h. To the rapidly stirred solution of 2-picolylithium, the methyl 4-alkoxybenzoate (1·5 mmol) in anhydrous ether (3 ml) was added dropwise. The reaction mixture was stirred overnight at ambient temperature and then gently heated at 40°C for 24 h. A solution of NH_4Cl (30 ml) was added to the cold reaction mixture until the solution became slightly basic (pH ~ 8). The organic phase was separated and the aqueous phase shaken with ether (3 × 30 ml). The combined ether extracts were dried over Na_2SO_4 and the solvent was removed under the reduced pressure. The crude products were purified by column chromatography on silica gel using toluene : ether (4·5 : 1·5) as eluent. Pure products **6 a–f**, **8** were obtained by a final crystallization from cyclohexane or *n*-hexane. The yields and NMR data are given in table 1.

4.4. *Preparation of copper(II) complexes 7 a–h, 11*

A solution of the free ligand (0.2 mmol) in a mixture of acetone : DMF (9 : 1, 4 ml) was heated briefly under reflux. Then, solid copper(II) acetate monohydrate (0·4 mmol) was added and the reaction mixture boiled for an additional 2 h. Upon cooling, brown crystals separated from the solution. The crystals were filtered off, washed with cold acetone and dried under reduced pressure. The structures of the copper complexes were confirmed by their IR spectra and elemental analysis.

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