

Insertion of unsaturations into the 1,4,7-triazacyclononane skeleton. Photochemical reaction between benzil and diethylenetriamine: synthesis and properties of 2,3-diphenyl-1,4,7-triazacyclonona-1,3-diene†

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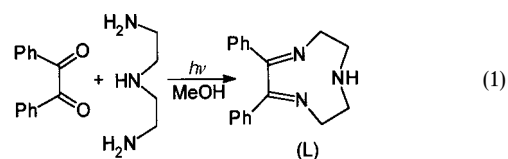
Photochemical reaction between benzil and diethylenetriamine (dien) in anhydrous methanol in the presence of oxygen yields a novel triaza macrocycle 2,3-diphenyl-1,4,7-triazacyclonona-1,3-diene (L). It was characterised by FTIR, EI mass and NMR (^1H and ^{13}C) spectra. A comparative study between the various physicochemical properties of L and the product (L_1 ; reported earlier by others) of the thermal reaction between benzil and dien is made in detail. L and L_1 can be regarded as isomers. While L_1 cannot be converted to L by UV radiation, L is transformed into L_1 upon refluxing in anhydrous methanol. The macrocycle L affords cationic copper(II) complexes of the type $[\text{CuL}]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-). Cyclic voltammetry and coulometry at platinum electrodes in dimethylformamide under an N_2 atmosphere show that the $\text{Cu}^{\text{III/I}}$ potential in $[\text{CuL}]\text{X}$ is 0.25 V vs. SCE. This indicates that L is a weak π -acid. L is photoluminescent in methanol at room temperature (emission maxima $\lambda_{\text{em}} = 380$ nm; quantum yield $\phi = 1.96 \times 10^{-2}$). Its emission when in the form of $[\text{CuL}]\text{X}$ in methanol is quenched considerably ($\lambda_{\text{em}} = 370$ nm; $\phi = 6.2\text{--}6.7 \times 10^{-3}$).

1,4,7-Triazacyclononane (tacn) is the simplest possible triaza macrocyclic ligand. It was first synthesised by Koyama and Yoshino in 1972.¹ Later many workers, especially Chaudhuri and Wiegardt, have developed its transition metal chemistry, which has proved to be as diverse as interesting.^{2,3} The situation can be summarised by saying that it coordinates “readily to metal ions producing stable complexes, many of which have unusual chemical and physical properties.”⁴ Subsequently, a number of derivatives of tacn have been synthesised to increase its dentition or to manipulate other properties of it. Their chemistry has been more fascinating; for some examples, see refs. 5–9. However, so far, no one has reported on the introduction of unsaturation(s) into the basic skeleton of tacn. With the expectation of generating some interesting chemistry, we have tried to introduce two imino N atoms in the tacn skeleton by reacting benzil with diethylenetriamine (dien). The results of the first phase of our experiments are reported here.

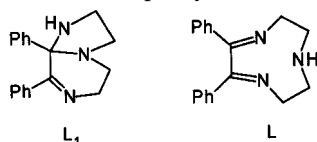
Results and discussion

In 1992, Okawara *et al.* reported that reaction of benzil and dien in equimolar proportion in ethanol yields 8,8a-diphenyl-1,2,3,5,6,8a-hexahydroimidazo[1,2-a]pyrazine (L_1) and not its macrocyclic isomer 2,3-diphenyl-1,4,7-triazacyclonona-1,3-

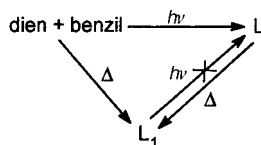
diene (L).¹⁰ This was verified later by X-ray crystallography.¹¹ Our AM1 calculations¹² using standard MOPAC package (version 1.10) indicate that L_1 is energetically lower than L in the gas phase by only 0.81 kcal mol⁻¹. Because of this small difference in the heats of formation of the two isomeric species, we decided to investigate the photochemical reaction between benzil and dien. We have found that when a moderately dilute solution of benzil and dien, taken in equimolar proportions, in anhydrous methanol is irradiated with UV light in the presence of air, L is obtained [eqn. (1)]. The



temperature at which the photochemical reaction is carried out is very crucial. It should be kept as low as possible; with rising temperature, the product is more and more contaminated with L_1 and above 50 °C, only L_1 is obtained. In the absence of oxygen, such as when reaction (1) is performed in an inert atmosphere, L is not formed at all irrespective of the temperature; the product is solely L_1 . Furthermore, when a solution of L_1 in anhydrous methanol is irradiated with UV light, one gets back L_1 only, that is L_1 is not converted to L upon irradiation. However, when L is refluxed in anhydrous methanol (the reaction condition used to synthesise L_1),¹³ L_1 is generated in moderate yield. These findings are summarised in Scheme 1. The role of oxygen in reaction (1) is, at present, not understood; some radicals seem to be involved in the process with the generation of $^1\text{O}_2$. On the other hand, the thermal conversion of L to L_1 appears to be a typical transannular cyclisation¹⁴ catalysed by a proton (Scheme 2), which



† Electronic supplementary information (ESI) available: the minimum energy structure of L as obtained by AM1 calculations together with some metric parameters and atomic charges. The DEPT 135 spectra of $\text{L} \cdot 1/3(\text{CHCl}_3)$ and L_1 in CDCl_3 . See <http://www.rsc.org/suppdata/nj/b0/b003967p/>



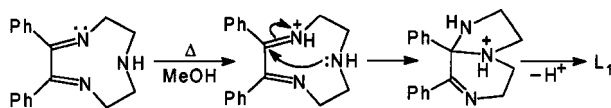
Scheme 1

comes from the protic solvent used. In our synthetic procedure, L is actually isolated as $L \cdot 1/3(\text{CHCl}_3)$ (see Experimental). The presence of CHCl_3 has been confirmed by a qualitative test for chlorine, CHN analyses and ^{13}C NMR (*vide infra*).

It is worth noting here that when dien is reacted with *m*-phthaldehyde in CH_3CN at room temperature in equimolar proportion, it yields a hexaaza macrocycle¹⁵ that has a complicated structure in the solid state; this macrocycle reacts with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ in CH_2Cl_2 to afford an orange, air-sensitive dinuclear copper(I) complex that has not been characterised structurally.¹⁵

In the IR spectra of L_1 , the C=N stretching frequency appears at 1629 cm^{-1} whereas this frequency in L is found to be slightly higher in energy at 1643 cm^{-1} . The C=N stretching frequency in $\text{R}_1\text{--N}=\text{C}(\text{R}_2)\text{--C}(\text{R}_2)=\text{N--R}_1$ occurs typically¹⁶ at 1640 cm^{-1} . Thus the IR spectra of L, especially when compared with that of L_1 , clearly indicates the presence of a 1,4-diaza-1,3-diene function in L.

Our AM1 calculations predict that L is not symmetric in the gas phase (Fig. S1 of ESI). This lack of symmetry prevails



Scheme 2

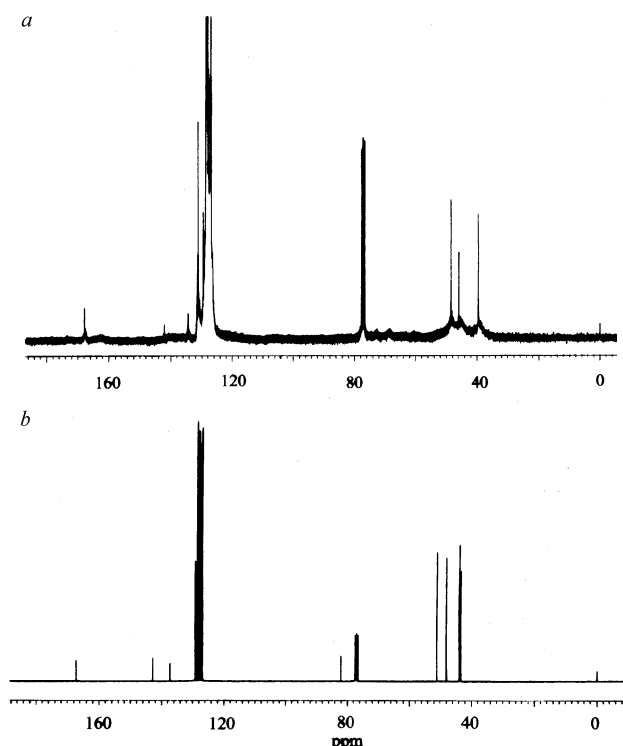


Fig. 1 300 MHz ^{13}C NMR spectrum of (a) $L \cdot 1/3(\text{CHCl}_3)$ and (b) L_1 in CDCl_3 (reference, TMS). The resonances around 77 ppm are due to the solvent. For the possible assignments of the various other resonances, see text.

at least in solution as evidenced by the ^{13}C NMR spectrum of L in CDCl_3 [Fig. 1(a)]. For comparison, the ^{13}C NMR spectrum of L_1 in CDCl_3 is also reproduced in Fig. 1(b). The most notable difference is that a quaternary alkyl C present in Fig. 1(b) at 82.08 ppm is absent in Fig. 1(a) as expected. Four methylene C atoms are observed (43.47, 43.82, 48.03 and 51.00 ppm) for L_1 in Fig. 1(b), while for L only three such resonances are observed (39.51, 45.75 and 48.40 ppm; two of the four methylene C atoms in L, possibly those bonded to the amino N, are found to be magnetically equivalent). The two imino C atoms of L resonate at 167.94 ppm, an expected position;¹⁷ however, the two quaternary aromatic C atoms are not magnetically equivalent—these appear separately at 131.31 and 142.07 ppm. In our AM1 calculations, the net charges on these two quaternary aromatic C atoms of L are not the same (*viz.*, -0.090 and -0.049). In the DEPT (dynamic enhancement by polarisation transfer) 135 spectrum [Fig. S2(a) of ESI], the presence of CHCl_3 (at 77.47 ppm) can be discerned very clearly.

There are two very significant differences in the chemical properties of L and L_1 . (i) While L cannot be hydrogenated by NaBH_4 in aqueous methanol at room temperature, under the same experimental conditions L_1 yields 2-(2,3-diphenylpiperazin-1-yl)ethylamine.¹³ (ii) L_1 disintegrates into benzil and dien when treated with an equimolar amount of H^+ (added in the form of perchloric acid) in methanol,¹⁸ whereas under the same conditions L remains intact.

Because of the presence of a 1,4-diaza-1,3-diene function, the macrocycle L is expected to be a π -acid and hence capable of preferentially stabilising the lower oxidation states of a transition metal. To assess this, we have initially tried to synthesise its copper(I) complexes. It is found that when L is reacted with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-) in equimolar proportions in anhydrous methanol under dry N_2 atmosphere, it affords brownish yellow copper(I) complexes of the formulation $[\text{CuL}]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-). These complexes are quite stable in air. In the solid state, they are stable for about a week, after which they slowly become grey. They are moderately soluble in methanol but dissolve well in dimethylformamide (DMF) giving rise to a brownish yellow colour; in solution these are stable for about an hour after which they gradually turn light green. It is noted that reaction of 1,4,7-trialkyl-tacn (tatacn) with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-) in tetrahydrofuran yields extremely air sensitive copper(I) complexes of the type $[\text{Cu}(\text{tatacn})(\text{CH}_3\text{CN})]\text{X}$ where acetonitrile is coordinated to the metal giving rise to $\text{Cu}^{\text{I}}\text{N}_4$ chromophores.¹⁹ Evidently our macrocycle L stabilises copper(I) much more than tacn against aerial oxidation.

The $\nu(\text{C}=\text{N})$ in $[\text{CuL}]\text{X}$ appears at $1632\text{--}1633\text{ cm}^{-1}$, which is lower in energy than that in the free ligand by $10\text{--}11\text{ cm}^{-1}$. This lowering is presumably due to π -back bonding between copper(I) and the 1,4-diaza-1,3-diene moiety in L. The $\nu(\text{N--H})$ in $[\text{CuL}]\text{X}$ is also quite different ($3406\text{--}3437\text{ cm}^{-1}$) from that (3311 cm^{-1}) in the free macrocycle. These observations support interaction of the metal with all three N atoms of L in $[\text{CuL}]\text{X}$. In solution, the complexes $[\text{CuL}]\text{X}$ behave as a 1 : 1 electrolytes, thereby excluding the possibility of anion coordination to the metal. Thus, a $\text{Cu}^{\text{I}}\text{N}_3$ chromophore is deemed to be present in $[\text{CuL}]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-). This $\text{Cu}^{\text{I}}\text{N}_3$ chromophore is quite inert towards addition reactions. It does not react with NO_2^- or PPh_3 in equimolar proportions in anhydrous methanol under an N_2 atmosphere to form adducts. On the other hand, NO_2^- and PPh_3 react with $[\text{Cu}(\text{tatacn})(\text{CH}_3\text{CN})]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-) resulting in substitution of the ligated acetonitrile moiety.¹⁹ It may be noted that though we have not been able to isolate any four-coordinate adduct of $[\text{CuL}]\text{X}$ in the solid state, coordination of solvents like acetonitrile, methanol or DMF in solution cannot be ruled out as the cuprous ion in $[\text{CuL}]^+$ moiety is quite exposed.

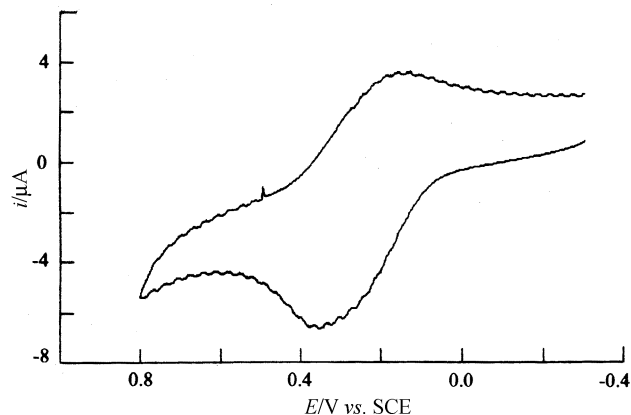
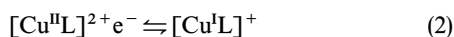


Fig. 2 Cyclic voltammogram of $[\text{CuL}]\text{PF}_6$ in DMF at a platinum electrode. Solute concentration, $1.23 \text{ mmol dm}^{-3}$; supporting electrolyte, 0.1 mol dm^{-3} tetraethylammonium perchlorate; scan rate, 0.050 V s^{-1} .

The electrochemical behaviour of $[\text{CuL}]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-) has been examined by cyclic voltammetry in DMF under N_2 atmosphere at a platinum electrode in the voltage range -0.4 to 0.8 V vs. SCE (saturated calomel electrode). For both the complexes, more or less identical (within experimental errors) quasi-reversible cyclic responses are obtained on the positive side of SCE (Fig. 2) with an average $E_{1/2}$ of 0.25 V vs. SCE and somewhat large peak-to-peak (ΔE_p) separations; ΔE_p increases from 0.2 V to 0.35 V as the scan rate is increased from 0.05 V s^{-1} to 1 V s^{-1} . Our coulometry at 0.6 V vs. SCE at a platinum wire gauge electrode in DMF under dry N_2 atmosphere establishes that the electrode process is oxidative and involves only one electron.† This implies that the couple observed at 0.25 V vs. SCE is $\text{Cu}^{\text{II/I}}$ [eqn. (2)]. So



far, to our knowledge, there is only one report (by Karlin *et al.*)²⁰ of the observation of a $\text{Cu}^{\text{II/I}}$ couple in a $\text{Cu}^{\text{I}}\text{N}_3$ chromophore, two of the three N atoms were pyridyl N and the other a secondary amino N. In Karlin's complex, which is air-sensitive, the $\text{Cu}^{\text{II/I}}$ couple has a potential of -0.08 V vs. SCE in DMF, which is significantly lower than that observed in our copper(II) complexes. We attribute this difference to the π -acidity of L, since at present it is quite well established that one of the main factors responsible for increasing the $\text{Cu}^{\text{II/I}}$

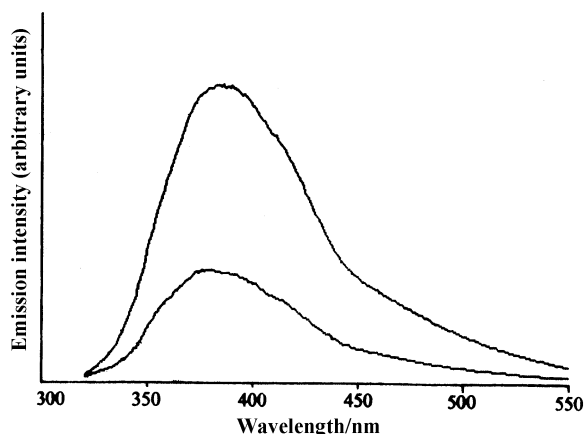


Fig. 3 Emission spectra of L (upper trace) and $[\text{CuL}]\text{ClO}_4$ (lower trace) in methanol at room temperature. Excitation wavelength, 300 nm . The absorbances of both the solutions at 300 nm are 0.58 .

† $[\text{CuL}]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-) samples ($3\text{--}4 \text{ mg}$) were electrolysed. Average coulomb count corresponded to 1.07 electron.

potential in copper complexes is the ligand π -acidity.^{21–23} Incidentally, no redox potential data for the complexes of the type $[\text{Cu}(\text{tatacn})(\text{CH}_3\text{CN})]\text{X}$ have been reported;¹⁹ however, considering their high sensitivity towards oxygen, the $\text{Cu}^{\text{II/I}}$ couple in these complexes is expected to occur at fairly negative potentials. L_1 , the non-macrocyclic isomer of L, also gives a cationic copper(II) complex (white in colour) of the formulation $[\text{CuL}_1]\text{ClO}_4$,¹⁸ which at a platinum electrode in DMF displays cyclic voltammograms characteristic of an adsorbed species ($E_{1/2} = -0.02 \text{ V vs. SCE}$).²⁴

Until now we have not been able to isolate any definite copper(II) complex of L. When L is reacted with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in $2:1$ molar proportion in methanol, a greenish paramagnetic complex containing metal and with the ligand moiety intact is obtained, but this could not be characterised. Reaction of L with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in methanol is not a clean process. On the other hand, while reaction of L_1 with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is not clean, L_1 reacts with $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ to afford blue $[\text{Cu}(\text{dien})(\text{CH}_3\text{COO})_n](\text{ClO}_4)_n$.²⁴ In contrast, the oxidised species in eqn. (2) has a bright yellow colour in DMF with absorption bands at 429 and 268 nm with ϵ values (calculated for $[\text{Cu}^{\text{II}}\text{L}]^{2+}$) of ~ 700 and $\sim 8200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively.

The macrocycle L shows a charge transfer band around 240 nm ($\epsilon = 2600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in its absorption spectrum in methanol. This band is shifted to a slightly longer wavelength in its copper(II) complexes; 250 nm ($\epsilon = 14400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in $[\text{CuL}]\text{ClO}_4$ and 246 nm ($\epsilon = 10200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in $[\text{CuL}]\text{PF}_6$. Upon excitation at 300 nm (within the charge transfer envelope) in methanol, the macrocycle L shows a single broad structureless emission around 380 nm (Fig. 3) with a quantum yield (ϕ) of 1.96×10^{-2} (*vs.* quinine sulfate²⁵ in $0.05 \text{ M H}_2\text{SO}_4$). This emission is strongly quenched in $[\text{CuL}]\text{X}$ in methanol with the emission maxima slightly blue shifted to 370 nm ; changing the anion has marginal effects on the fluorescence quantum yield [ϕ for $[\text{CuL}]\text{ClO}_4$ is 6.7×10^{-3} (Fig. 3) and that for $[\text{CuL}]\text{PF}_6$ is 6.2×10^{-3}]. Interestingly, in $[\text{CuL}_1]\text{ClO}_4$, the copper(II) complex of L_1 , the fluorescence quantum yield of the fluorophore L_1 is increased eight-fold.¹⁸ For a complete comparison, it is noted that L_1 has an emission maximum at 383 nm in methanol with a ϕ of 1.0×10^{-3} . While quenching of the fluorescence of an organic fluorophore by transition metal ions is a very common phenomenon as observed here, $[\text{CuL}_1]\text{ClO}_4$ presents one of the rare cases¹⁸ where a transition metal ion induces enhancement of the fluorescence of an organic fluorophore.

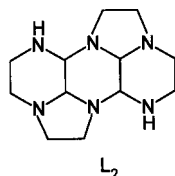
Concluding remarks

Here we have demonstrated that by reacting dien with benzil in anhydrous methanol under UV radiation, two imino N atoms can be introduced into the basic skeleton of 1,4,7-triazacyclononane, resulting in a novel triaza macrocycle L. The presence of oxygen is essential in the formation of L. However, the mechanism by which oxygen brings about the reaction is at present not clear. The physicochemical properties of L are very different from those of L_1 which is produced by carrying out the reaction between benzil and dien thermally. L and L_1 can be regarded as isomers. The macrocycle L can be thermally converted to the non-macrocyclic L_1 . This result is expected from our AM1 calculations, as they indicate that L is energetically higher than L_1 even if by only *ca.* 1 kcal mol^{-1} .

The magnitude of the $\text{Cu}^{\text{II/I}}$ potential in $[\text{CuL}]\text{X}$ ($\text{X} = \text{ClO}_4^-$ and PF_6^-) shows that L stabilises copper(II) more than copper(II) though not to any great extent. Thus, L can be designated as a weak π -acid. It can be used to stabilise to

some extent low oxidation state(s) of a transition metal. The π -acidity in L arises because of the presence of the 1,4-diaza-1,3-diene function in L. The π -acid-like behaviour of L is also apparent from the fact that the C=N stretching frequencies in the copper(I) complexes are less than that in the free macrocycle by 10–11 cm^{-1} . In any case, it is clear from our studies that L stabilises copper(I) much more than tacn.

It is appropriate to mention here that the thermal reaction between dien and glyoxal gives rise to L_2 , which is quite different from L_1 in nature.²⁶ Hence, our studies have been restricted here to the reaction of dien with benzil only. However, at present we are engaged in investigating the reactions of dien with phenanthroquinone.



Experimental

General

$[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ were synthesised by literature methods.^{27,28} Fresh analytical reagent grade DMF (purchased from S. D. Fine-Chem Ltd., India) was used directly for electrochemistry. All other reagents were procured commercially. Copper was estimated gravimetrically as CuSCN . Microanalyses were performed using a Perkin-Elmer 2400II elemental analyser. Molar conductance was measured by a Systronics (India) direct reading conductivity meter (model 304). Melting points were determined by a melting point apparatus procured from CBC Power System (Calcutta, India) and are uncorrected. IR spectra (KBr disc) were recorded on a Nicolet Magna-IR spectrophotometer (Series II), UV-VIS spectra on a Shimadzu UV-160A spectrophotometer, ^1H and ^{13}C NMR spectra by a Bruker DPX300 spectrometer and EI (electron impact) mass spectrum on an AEI MS 30 instrument. All the photoluminescence studies were carried out in air using a Spex Fluorolog spectrofluorimeter. Cyclic voltammetry and coulometry were performed using EG&G PARC electrochemical analysis system (model 250/5/0) in DMF under a dry nitrogen atmosphere in conventional three-electrode configurations with tetraethylammonium perchlorate as the supporting electrolyte. An ECDA-Pt02 platinum disk electrode procured from Con-Serv Enterprises, India was used as the working electrode in cyclic voltammetry. Under the experimental conditions employed here, the ferrocene-ferrocenium couple appears at 0.402 V vs. SCE with an ΔE_p of 95 mV at a scan rate of 0.050 V s^{-1} .

Syntheses

$L \cdot 1/3(\text{CHCl}_3)$. A solution of 2.68 g (12.8 mmol) of benzil and 1.4 ml (12.8 mmol) of diethylenetriamine in 110 ml of anhydrous methanol was irradiated in a thermostated Pyrex vessel using a Hanovia 450W mercury lamp for 6 h (the temperature of the reaction mixture was below 18 °C). Then the solvent was removed under reduced pressure to obtain a red viscous liquid, which was loaded on a silica gel (60–120 mesh) column (30 \times 2.5 cm) and eluted successively with chloroform and methanol. The chloroform fraction, after work-up, afforded white crystals of L_1 (1.16 g, 33%). From the methanol fraction, evaporation of the solvent under reduced pressure at room temperature yielded a thick red liquid, which was dissolved in 25 ml of chloroform and washed thoroughly with distilled water (75 ml \times 3). The reddish yellow aqueous layer was discarded. The yellow chloroform layer was evaporated at room temperature under reduced pressure to \sim 5 ml and then kept *in vacuo* over fused CaCl_2 to obtain a fluffy yellow com-

pound. Yield: 1.12 g (28%); mp 70 °C; found: C, 69.48; H, 6.15; N, 13.19. $\text{C}_{18.333}\text{H}_{19.333}\text{N}_3\text{Cl}$ requires C, 69.40; H, 6.15; N, 13.25%. EI MS: m/z 277 (L^+ , 10%). FTIR/ cm^{-1} (KBr): 3311m (N–H), 1643vs (C=N). ^1H NMR (300 MHz, CDCl_3 , TMS): 2.73–4.09 (10, $-\text{CH}_2-$ 8H); 7.18–7.67 (several br, m 10.333H); NH not observed. UV-VIS $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH_3OH): 240 (2600).

Conversion of L to L_1 . $L \cdot 1/3(\text{CHCl}_3)$ (1.0 g, 3.2 mmol) was refluxed in 10 ml of anhydrous methanol for 6 h. Then it was left in air for 2 h. White crystals of L_1 deposited, which were filtered off, washed with 2 ml of cold methanol and dried *in vacuo* over fused CaCl_2 . Yield, 0.22 g (24%); mp 142 °C.

$[\text{CuL}]\text{ClO}_4$. Solid $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ (0.33 g, 1 mmol) was added to 0.32 g (1 mmol) of $L \cdot 1/3(\text{CHCl}_3)$ dissolved in 25 ml of anhydrous, degassed methanol under a dry N_2 atmosphere and stirred for 3 h. The brownish yellow compound precipitated was filtered off, washed with 2 ml of methanol and dried *in vacuo* over fused CaCl_2 . Yield, 0.19 g (43%); found: C, 49.04; H, 4.41; N, 9.49; Cu, 14.42. $\text{C}_{18}\text{H}_{19}\text{N}_3\text{CuClO}_4$ requires C, 49.07; H, 4.35; N, 9.54; Cu, 14.43%. FTIR/ cm^{-1} (KBr): 3406br (N–H), 1633s (C=N), 1098vs, 623m (ClO_4). $A_M(\text{CH}_3\text{OH})$: 92 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (1 : 1 electrolyte). UV-VIS $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH_3OH): 355 sh (2050), 250 (14 400) and 218 (21 600). UV-VIS $\lambda_{\text{max}}/\text{nm}$ (Nujol mull): 350 and 285.

$[\text{CuL}]\text{PF}_6$. This was synthesised by a procedure exactly similar to that described for $[\text{CuL}]\text{ClO}_4$ by starting with 0.37 g (1 mmol) of solid $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$. Yield, 0.17 g (35%); found: C, 44.51; H, 3.90; N, 8.68; Cu, 13.09. $\text{C}_{18}\text{H}_{19}\text{N}_3\text{CuPF}_6$ requires C, 44.48; H, 3.95; N, 8.65; Cu, 13.08%. FTIR/ cm^{-1} (KBr): 3437br (N–H), 1632s (C=N), 841vs (PF_6). $A_M(\text{CH}_3\text{OH})$: 110 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (1 : 1 electrolyte). UV-VIS $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) (CH_3OH): 350sh (1200), 246 (10 200) and 211 (21 000). UV-VIS $\lambda_{\text{max}}/\text{nm}$ (Nujol mull): 352, 290, 255.

Caution! Although we have not encountered any problems in handling the perchlorates, it is noted that perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions.

Acknowledgements

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