Novel polypyridyl ruthenium(II) complexes containing oxalamidines as ligands

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Abstract

The complexes [Ru(bpy) 2(H 2 TPOA)](PF 6 ) 2·4H 2 O (1); [Ru(Me-bpy) 2(H 2 TPOA)](PF 6 ) 2·2H 2 O (2); [Ru(bpy) 2(H 2 TTOA)](PF 6 ) 2·2H 2 O (3); [Ru(Me-bpy) 2(H 2 TTOA)](PF 6 ) 2·2H 2 O (4) and {[Ru(bpy) 2(TPOA)](PF 6 )} 2·2H 2 O (5) (where bpy is 2,2'-bipyridine; Me-bpy is 4,4'-dimethyl-2,2'-bipyridine; H 2 TPOA is N,N',N'',N'''-tetraphenyloxalamidine; H 2 TTOA is N,N',N'',N'''-tetratolyloxalamidine) have been synthesised and characterised by 1H NMR, FAB MS, infrared spectroscopy and elemental analysis. The X-ray investigation shows the coordination of the still protonated oxalamidine moiety via the 1,2-diimine unit. The dimeric compound (5) could be separated in its diastereoisomers (5') and (5") by repeated recrystallisation. The diastereomeric forms exhibit different 1H NMR spectra and slightly shifted electronic spectra. Compared with the model compound [Ru(bpy) 3] 2+, the absorption maxima of (1)–(5) are shifted to lower energies. The mononuclear complexes show Ru(III)/II-couples at about 0.9 V versus SCE, while for the dinuclear complex two well defined metal based redox couples are observed at 0.45 and 0.65 V, indicating substantial interaction between the two metal centres. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemistry; Ruthenium complexes; Oxalamidines complexes; Polypyridyl complexes

1. Introduction

Oligonuclear polypyridyl Ru(II) complexes are being investigated currently in detail because of their rich electrochemical and photophysical properties which render them very attractive systems for modelling electron and energy transfer processes [1], which are known to play a crucial role in biological processes such as respiration, photosynthesis and oxidative DNA cleavage [2].

In most of the compounds described so far, the Ru(II) metal centre is bound to aromatic and polyaromatic pyridyl compounds containing 1,2-diimine units [3]. Less attention has been paid to compounds containing ligands in which the chelating 1,2-diimine unit is not part of an aromatic system [4] [5]. In this contribution novel ruthenium polypyridyl complexes containing nonaromatic 1,2-diimines are further considered and we report our studies on mono- and dinuclear Ru(II) complexes containing N,N',N'',N'''-tetraaryloxalamidines (aryl = phenyl:H 2 TPOA; aryl = tolyl:H 2 TTOA). (For structures of these ligands see Fig. 1.)

The purpose of these investigations is to study the effect that these non-aromatic dimine ligands have on the absorption spectra and the electrochemical properties of ruthenium polypyridyl moieties. Also of interest is the determination of the coordination mode of the ligands. Since oxalamidines can be deprotonated [9], several coordination modes are possible for this type of ligand. The acid–base properties of the ligands can in principle also be used to tune the electronic properties of the ruthenium polypyridyl complexes obtained. The coordination chemistry of these ligands with complex fragments such as Mo(CO) 6; BR 2 (R = Me); and Cu(I)L has already been reported [6–8].
H₂TPOA and H₂TTOA were prepared according to literature procedures [10]. RuCl₃·xH₂O was purchased from Strem Chemical and used without further purification. 2,2ʹ-bipyridine and 4,4ʹ-dimethyl-2,2ʹ-bipyridine were obtained from Aldrich.

2.2. Instrumentation and measurements

¹H NMR spectra were obtained on a Bruker AC 200 MHz spectrometer and all spectra were referenced to TMS or deuterated solvent as an internal standard. UV–Vis spectra were recorded on a Shimadzu UV 3100 spectrometer using Teflon stopped quartz cells having a path length of 1 cm. FAB MS data were obtained on a Finnigan MAT SSQ 710 instrument using 2,4-dimethoxybenzylalcohol as a matrix. Studies of the acid–base properties were carried out in a 50/50 (v:v) mixture of acetonitrile and Britton–Robinson buffer (0.04 M H₃BO₃; 0.04 M H₃PO₃; 0.04 M CH₃COOH). This mixture was used for all measurements and the pH was measured directly with an EDT microprocessor pH-meter calibrated with standard buffers of pH 4.0 and 7.0. The pKₐ constants were obtained from the absorption spectra with the aid of a diagram ΔAbs% versus pH. The electrochemical cell was a conventional three compartment cell. The reference electrode was a saturated calomel electrode and the working electrode was a 3 mm diameter Teflon shrouded glassy carbon electrode and a platinum gauze was used as the counter electrode. A solution of 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile was used as the electrolyte in all measurements. Cyclic voltammetry was carried out on a CH-instruments model 660 electrochemical workstation interfaced to an Elonex PC466 personal computer. Analytical HPLC experiments were carried out using a Waters HPLC system, consisting of a model 501 pump, a 20 µl injector loop, a Partisil SCX radial PAK cartridge mounted in a radial compression Z module and a Waters 990 photodiode array detector. The system was controlled by a NEC APC III computer. The detection wavelength was 290 nm. The mobile phase used was 90:10 CH₃CN:H₂O containing 0.1 M LiClO₄.

2.3. Preparations

A typical protocol for preparation of compounds 1–4 is as follows (described here for [Ru(bpy)₂(H₂TPOA)](PF₆)₂·2H₂O (1)): 0.416 g (0.8 mmol) of Ru(bpy)₂Cl₂·2H₂O were dissolved in 50 ml ethanol–water (95:5 v/v%) and subsequently 0.390 g (1.0 mmol) of H₂TPOA was added. The mixture was refluxed for 24 h, during which the colour changed from violet to deep red. After cooling to room temperature (r.t.), the solution was evaporated to dryness. The resulting residue was redissolved in a small amount of acetonitrile and purified using column chromatography (Al₂O₃; acetonitrile–toluene). The brick red main band was collected and the complex precipitated by adding an excess of aqueous NH₄PF₆. The precipitate was isolated, washed with diethylether and dried under vacuum. Alternatively, the pure compounds can be also obtained by fractional crystallisation from acetonitrile–water.

[Ru(bpy)₂(H₂TPOA)](PF₆)₂·2H₂O (1): yield: 84%. ¹H NMR (DMSO-d₆, δ, ppm, 20°C): 10.02 (s, NH, 2H); 9.23 (d, H°, 2H); 8.42 (d, H₂, 2H); 8.24 (t, H 4, 2H); 8.12 (d, H², 2H); 8.05 (t, H², 2H); 7.71 (t, H², 2H); 7.47 (d, H°, 2H); 7.19 (t, H², 2H); 6.96 (t, H₆, 4H); 6.83 (d, H₆, 4H); 6.78 (t, H₆, 2H); 6.56; 6.49; 5.31 (dynamic system, H₆, 10H). FAB MS (dmba, m/z): 949 ([M⁺]–PF₆⁻); 804 ([M⁺]–2PF₆⁻). IR [Nujol; ν, cm⁻¹]: 3382 (m, NH); 3075 (w, arom. C), 842, 557 (s, PF₆⁻). UV–Vis (acetonitrile, λMLCT, nm): 469 (ε = 13938 l cm⁻¹ mol⁻¹). CV (acetonitrile, 0.1 M TEAP versus SCE, E_Ru(III/II,UP)V): 0.94; Anal. Calc. C, 48.89; H, 3.75; N, 9.92. Found: C, 48.49; H, 3.95; N, 9.88%.

[Ru(Me-bpy)₂(H₂TPOA)](PF₆)₂·2H₂O (2): yield: 75%. ¹H NMR (DMSO-d₆, δ, ppm, 20°C): 9.98 (s, NH, 2H); 9.32 (d, H°, 2H); 8.42 (d, H₂, 2H); 8.11 (d, H², 2H); 7.96 (t, H², 2H); 7.54 (d, H°, 2H); 7.14 (t, H², 2H); 7.00 (t, H₆, 2H); 6.99 (t, H₆, 4H); 6.79 (d, H₆, 4H); 6.57; 6.45; 5.37 (dynamic system, H₆, 10H); 2.69 (s, CH₃, 6H); 2.34 (s, CH₃, 6H). FAB MS (dmba, m/z): 1005 ([M⁺]–PF₆⁻); 859 ([M⁺]–2PF₆⁻–H⁺). IR [Nujol; ν, cm⁻¹]: 3367 (m, NH); 3060 (w, arom. C–H); 2924 (w, C–H); 1619 (s, C=N); 1450 (s, C=C), 845, 558 (s, PF₆⁻). UV–Vis (acetonitrile, λMLCT, nm): 476 (ε = 11728 l cm⁻¹ mol⁻¹). CV (acetonitrile, 0.1 M TEAP versus SCE, E_Ru(III/II,UP)V): 0.90; Anal. Calc. C, 52.20; H, 4.03; N 9.78. Found: C, 51.88; H, 4.92; N, 8.74%.

2.4. Characterization

2.4.1. X-ray crystallography

The X-ray crystallographic data for compound 3 were collected at 100 K on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation (λ = 0.7107 Å) in the w扫描 mode. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F² using the SHELXTL program package. The non-hydrogen atoms were refined anisotropically.

2.4.2. Electronic spectra

The electronic spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. The ligands were dissolved in acetonitrile to give a concentration of 1 mM. The spectra were recorded in the UV–Vis region (190–800 nm).

2.4.3. Mass spectrometry

FAB mass spectra were recorded on a JEOL JMS-DX300 spectrometer using Teflon stoppered quartz cells (diameter: 3 mm). The matrix was 2,4-dimethoxybenzylalcohol. The samples were dissolved in acetonitrile and diluted by diethylether.

2.4.4. NMR spectroscopy

¹H NMR spectra were recorded on a Bruker AC 200 MHz spectrometer and all spectra were referenced to TMS or deuterated solvent as an internal standard. The spectra were obtained in DMSO-d₆, CDCl₃ or D₂O at room temperature. The spectra were recorded using 90 and 100 MHz spectrometers.

2.4.5. FT-IR spectroscopy

FT-IR spectra were recorded on a Bruker IFS 113v spectrometer using the KBr pellet technique.

2.4.6. UV–Vis spectroscopy

UV–Vis spectra were recorded on a Shimadzu UV-2401PC spectrophotometer using Teflon stopped quartz cells having a path length of 1 cm. The samples were dissolved in acetonitrile or dichloromethane.

2.4.7. Microanalysis

Microanalytical Laboratory of the University College Dublin and at the Friedrich–Schiller-University, Jena.
2H), 7.08 (t, H, 2H); 6.57 (dd, H arom, 8H); 6.08; 5.49; (dynamic system, H arom, 8H); 2.00 (s, CH3, 6H); 1.80 (s, CH3, 6H). FAB MS (dmba, m/z): 1061 ([M+1] − PF6− + H+); 860 ([M]+ − 2PF6−). IR (Nujol; ν, cm−1): 3366 (m, NH); 2923 (w, C–H); 1593 (s, C–N); 1463 (s, C=C); 841, 557 (s, PF6−). CV (acetonitrile, 0.1 M TEAP versus SCE, E(RuIII/II, V)) : 0.96. UV–Vis (acetonitrile, λMLCT, nm): 478 (ε = 11274 1 cm−1 mol−1); Anal. Calc. C, 54.42; H, 4.25; N, 9.44. Found: C, 50.91; H, 4.94; N, 8.66%.

\[ \text{[Ru(Me-bpy)}(\text{H2TTOA})\text{]}(\text{PF6})\text{2·2H2O (4), yield: 45%}. \]

A total of 195 mg (0.5 mmol) of TPOA were dissolved in 60 ml ethanol–water (50:50 v/v). An excess of 0.671 g (0.8 mmol) of Ru(bpy)2Cl2·2H2O was added and the resulting solution was refluxed for 8 h. The reaction mixture was treated with an excess of aqueous NH4PF6. The precipitate was redissolved in acetone–water and the resulting solution was refluxed for 8 h. The water and pure and mixed fractions of the pair (compound and the unresolved (DL and LL) fractional crystallisation. Yield: 1.3 g (84%) of (5). 3F).

\[ \text{[Ru(bpy)}\text{2(TPOA)}\text{]}(\text{PF6})\text{2·2H2O (5).} \]

X-ray diffraction was carried out on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation and φ-scan technique (Δφ = 1°, scan range 180°, time/frame = 30 s) at 20°C. Data were corrected for Lorentz and polarisation effects, but not for absorption [13].

The structure was solved by direct methods (SHELX [14]) and refined by full-matrix least-squares techniques against F2 (SHELXL-93 [15]). The hydrogen atoms (without the water molecules) were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

### 3. Results and discussion

#### 3.1. Synthesis and structure of mononuclear complexes 1–4

The synthesis of ruthenium oxalamidine compounds was accomplished using standard methods. The nuclearity of resulting complexes could be governed by controlling the metal to ligand ratio (see Fig. 2). Nevertheless, in the case of the mononuclear compounds 1–4 some dimer formation could not be prevented and subsequently cleaned by column chromatography. The 1H NMR spectra do exhibit the expected pattern of the bpy protons in a C3-symmetric Ru(bpy)2 environment. All protons of the bipyrindine ligands could be attributed unambiguously by 1H–1H-COSY experiments.

The signals that can be attributed to the aromatic substituents of the coordinated oxalamidine ligands are found at a higher field than the bipyrindine protons. At r.t., only half of the expected aromatic signals for 1–4 are well resolved peaks (see for example compound 3 in Fig. 3). Thus, compound 3 shows for half of the tolyl protons at r.t. one well resolved AA'BB' spin system, while the other half is observed as a broadened signal at about 6.0 ppm. Upon heating, this signal becomes the expected AA'MM' spin system at 5.49 and 6.08 ppm. This dynamic process is most likely explained by hindered rotation of the aryl substituents on the oxalamidine ligands. Interestingly, this behaviour is not observed in the binuclear compound 5 (vide infra). This can be explained by enhanced crowding around the complex.
tetraphenyloxalamidine bridging ligand, not allowing for any rotation of the aryl substituents around the C–N bound.

An important aspect of this study is establishing the coordination mode of the oxalamidine ligand. The tetradentate nature of these ligands allows different coordination modes (see Fig. 4) and possible deprotonation of the ligands also needs to be considered.

The presence of protonated secondary amino functions in the mononuclear complexes 1–4 was established from $^1$H NMR measurements, by infrared spectroscopy and by elemental analysis. This protonation behaviour is contrary to that of triazole ligands, where a secondary N–H function is being deprotonated upon coordination [11]. The composition of compounds 1–4 was further confirmed by FAB MS, in which the complexes exhibit characteristic losses of the only electrostatically bound PF$_6^-$ anions rendering the cationic complex fragment as the most intense signal (see Section 2).

Fig. 2. Synthesis of mononuclear complexes 1–4 and dimeric complex 5.

Fig. 3. $^1$H NMR spectra of [(bpy)$_2$Ru(H$_2$TTOA)](PF$_6$)$_2$·2H$_2$O (3), at 293 and 383 K exhibiting the dynamic behaviour of the aromatic protons of the tetratolyloxalamidine.
In order to establish the coordination mode of the ligand, the X-ray structure of complex 1 was determined. Some relevant distances and angles are given in Table 1. As in solution, complex 1 exhibits C₂-symmetry in the solid state. The result of the X-ray investigations depicted in Fig. 5 demonstrates clearly octahedral coordination of the Ru(II) ion by two bipyridine ligands and by one H₂TPOA ligand. The latter ligand is coordinated via the 1,2-diimine unit. The secondary amines are clearly protonated. The C–N(H) bond length (d_{C–N} = 1.355(5) Å) reveals a partial double bond character probably due to the delocalisation of the double bond in the amidine system, but the 1,2-diimine unit is defined clearly by its significantly shorter C–N distance (d_{C–N} = 1.294(4) Å). This allows one to draw the unambiguous conclusion, that the tetraphenyloxalamidine is coordinated via its 1,2-diimine system (C in Fig. 4). It is worth emphasising that H₂TPOA is bonded in its s-cis configuration while the free ligand exists in crystal form only, as a s-trans conformer [12].

The Ru–N(bpy)-distances (d_{Ru-N} = 2.049(3)–2.053(3) Å) are in the typical range of other members of the Ru(bpy)₂ (LL)-class [2], while the Ru–N(oxalamidine) distances are elongated slightly (d_{Ru-N} = 2.081(3) Å) indicating the weaker back bonding character of the oxalamidine ligand or maybe a steric hindrance by the phenyl groups. Interestingly the Ru–N distance in the, also neutral, dihydrazone type ligands are significantly shorter at 2.01 Å [4]. The N–Ru–N bite angles show the anticipated values (α = 78.7(1)°) for the bipyridines, while the bite angle of the oxalamidine do not exceed α = 75.4(2)° due to easier pinching of the non rigid oxalamidine system.

In addition, the X-ray investigations reveal intermolecular interactions. In the crystalline state compound 1 forms a polymeric chain of alternating ordered

**Table 1**

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>Angle (°)</th>
</tr>
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<tr>
<td>Ru–N(4)</td>
<td>2.049(3)</td>
</tr>
<tr>
<td>Ru–N(3)</td>
<td>2.053(3)</td>
</tr>
<tr>
<td>Ru–N(1)</td>
<td>2.081(3)</td>
</tr>
<tr>
<td>N(1)–C(1)</td>
<td>1.294(4)</td>
</tr>
<tr>
<td>N(2)–C(1)</td>
<td>1.355(5)</td>
</tr>
<tr>
<td>C(1)–C(1A)</td>
<td>1.503(6)</td>
</tr>
<tr>
<td>O(1)–O(2)</td>
<td>2.778(5)</td>
</tr>
<tr>
<td>O(1)–O(2A)</td>
<td>2.862(5)</td>
</tr>
</tbody>
</table>

*Fig. 4. Possible coordination modes of the oxalamidine ligand towards the Ru(bpy)₂ moiety.*

*Fig. 5. Drawing of the X-ray structure of [(bpy)₂Ru(H₂TPOA)(PF₆)₂]·4H₂O (1) (anions and solvent molecules are omitted for reasons of clarity).*
3.2. Synthesis and structure of the dinuclear compound \([\{\text{Ru(bpy)}_2\text{(TPOA)}\}_2(\text{PF}_6)_2\cdot 2\text{H}_2\text{O}\} (5)\)

The use of more than twofold excess of \(\text{Ru(bpy)}_2\)-precursor yields the dinuclear compound (5) in good yield. HPLC measurements indicate the presence of two compounds with a peak area of 50:50%. It was possible to separate these by recrystallisation in acetone–water (60/40 v/v%). Elemental analysis yielded identical compositions for both compounds and was indicative of a deprotonation of the tetraphenyloxalamidine ligand in both cases. The \(^1\text{H}\) spectra of the two fractions were recorded in DMSO-\(d_6\) and are depicted in Fig. 7. The spectra are only slightly different and exhibit a quite simple pattern with only one set of aromatic phenyl signals as expected for a high symmetrical complex. All peaks could be assigned unequivocally with the help of COSY experiments. No broad peaks, as in the mononuclear compounds, appear in the spectra and the phenyl rings of the TPOA\(^2\)-bridging ligand show only one well-resolved set of two triplets and one doublet. This suggests that in the dinuclear compound, the aryl rings are not free to rotate. The protons of the bipyridine ligands show the usual shifts and pattern.

On the basis of these observations, it seems reasonable to assume that the two fractions are optical isomers (5%) and (5%). The presence of stereoisomers is related to the well-known stereochemical problem of linking two metal ions with helical chirality by a bridging ligand [17]. This causes the emergence of one meso-form (\(\text{AA}\)) and one enantiomeric pair with \(\text{AA}\) and \(\text{AA}\) configuration. The two isolated diastereomeric isomers (5') and (5'') should correspond to the meso-(\(\text{AA}\))-compound and to the unresolved (\(\text{AA}/\text{AA}\)) enantiomeric pair (enantiomers are indistinguishable in \(^1\text{H}\) NMR spectroscopy) [18], but with the data available it was not possible to assign the absolute configuration of (5') and (5'').

3.3. Absorption spectra

The absorption spectra of compounds 1–5 were recorded in methanol–ethanol and show the typical
features for members of the polypyridyl ruthenium(II) class. The results are summarised in Table 2. The most significant feature of these spectra is a strong band in the visible range due to dπ–π*-MLCT transitions [19].

In comparison to the model compound [Ru(bpy)₃]²⁺ (λ_{MLCT} = 452 nm), the MLCT bands of the oxalamidine complexes exhibit a shift to lower wavenumbers. Therefore, it can be suggested that the investigated oxalamidines possess stronger σ-donor and weaker π-acceptor properties than bipyridine. The presence of methylsubstituents in compounds 2 and 4 has only a minor influence on the absorption maxima. The MLCT-maximum of the dinuclear compound is observed at a lower energy than in the monomeric compounds. This reflects the deprotonation of the bridging ligand and it is indicative of the stronger σ-donor and weakened π-acceptor properties of the deprotonated bridge.

The possibility of tuning the absorption spectra of the compounds 1–4 by changing the acidity of the solution was investigated. Thus, Fig. 8 shows the absorption spectra of compound 1 in the range from pH 3.08 to 12.05. In this range, only one set of isobestic points is found. The MLCT band around λ = 470 nm collapses gradually upon deprotonation and two new bands appear. The emerging band at λ = 505 nm can be assigned to a MLCT transition in the deprotonated complex. The deprotonated tetraphenyloxalamidine ligand should act as a stronger σ-donor and increasing electron density around the metal shifts the maximum of the MLCT band to higher wavelengths. The band at λ = 380 nm might correspond to an additional MLCT band to either bpy or to H₂TPOA.

From the absorption spectra it was possible to determine the pKₐ values for compounds 1–4 (see Table 2). The pKₐ is relatively insensitive to substitution changes on both the bpy ligand and the oxalamidines. Only one protonation step could be observed in the range measured for all complexes. This might suggest that both N–H functions are deprotonated at the same time or that the second deprotonation is outside the range measured.

The two diastereomers (5') and (5'') show slightly different absorption spectra (see Fig. 9). Potential differences in the electronic behaviour of diastereomeric and enantiomeric isomers of polypyridyl ruthenium(II) complexes were the subject of several recent investigations [20,21]. Multinuclear ruthenium polypyridyl complexes will normally contain a manifold of diastereomers and these studies are aimed at determining whether optical isomers have significantly different photophysical properties. That is a rather important problem, because constructing antenna systems from Ru–bipyridyl units demands the very strict control of the photophysical properties of such light absorbing devices.

Surprisingly, the measurement of compounds 1–5 does not show any emission. Even cooling down to 77 K in various solvents and extended change of the pH-value did not render the expected emission. This is an unexpected result, because the appearance of a emission from a long living 3MLCT state is to be seen as one of the intrinsic characteristics for polypyridyl–Ru(II) compounds. One possible explanation might be that the electron occupies an oxalamidine π*-orbital instead of a bipy π*-orbital in the excited state. Thus, the inappropriateness of the oxalamidine π*-orbitals to deliver a long living excited state could explain the absence of emission. This assumption might be supported by the first reduction potentials for compounds 1–4 which are irreversible, in contrast to those of polypyridyl–Ru(II) complexes.

3.4. Electrochemistry

The Ru(III)/(II) potentials for the PF₆-salts in 0.1 M solution of tetra-n-butylammonium perchlorate in acetonitrile versus saturated calomel electrode are sum-
marised in Table 2. In comparison with [Ru(bpy)]32+ (E_{II/III} = 1.23 V vs. SCE) all redox Ru(III/II) couples of the mononuclear complexes 1–4 are shifted to more negative potentials (E_{II/III} = 0.96–0.87 V), in agreement with an increased electron density around the ruthenium ion caused by the better $\sigma$-donor properties of the oxalamidine ligands. Methyl substitution on the aromatic 1,2-diimine ligands in polypyridyl ruthenium(II) chemistry. The structure of the mononuclear complexes of the type [Ru(bpy)2(LL)]2+ was elucidated by $^1$H NMR, FAB MS and X-ray structure determination of compound 13. On supramolecular architectures. Future research efforts will follow this line.

5. Supplementary material

Further details of the crystal investigations are available on requests from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the depository number CCDC 13099, the names of the authors, and the journal citation.

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