DALTON
FULL PAPER

Metal-directed self-assembly of terphenyl based dithiocarbamate ligands

Lindsay H. Uppadine, Jennifer M. Weeks and Paul D. Beer *

Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: paul.beer@chem.ox.ac.uk

Received 19th July 2001, Accepted 24th September 2001
First published as an Advance Article on the web 19th October 2001

The synthesis of dithiocarbamate ligands based on an *m*-terphenyl scaffold is reported. These ligands self-assemble with zinc(II), nickel(II) and copper(II) ions to afford neutral, dinuclear metallomacrocycles in varied yields. The assemblies have been characterised by a range of techniques, including ^{1}H NMR, ^{13}C NMR and UV-vis spectroscopy, elemental analysis, mass spectrometry and cyclic voltammetry. Intramolecular coordination of bipyridyl guests has been investigated with the zinc(II) containing macrocycles. NMR spectroscopy and FAB mass spectrometry demonstrate the formation of 1 : 1 inclusion complexes with 4,4′-bipyridyl.

Introduction

The metal-directed self-assembly of polydentate ligands is a well-established area of coordination chemistry.[1] This synthetic methodology provides access to well-defined supramolecular architectures based on coordinative interactions. Examples to date span a range of inorganic assemblies including helicates,[2] cages,[3] ladders,[4] racks[5] and grids.[6]

Metal-directed self-assembly presents several advantages over conventional covalent syntheses.[1,7] For example, only a few basic subunits are required, which can be assembled in just one or a few steps. The construction process can be readily controlled because it employs reversible bonds. This allows for error-recovery and structural changes according to environment. In addition, metal ions provide a range of coordination geometries, binding strengths/labilities and photochemical/redox properties which can be exploited in self-assembly.

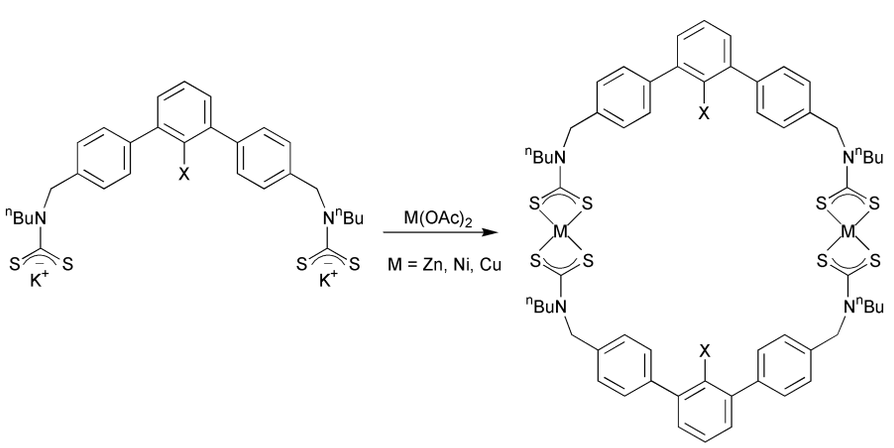
This paper details the synthesis of dinuclear macrocycles based on metal–dithiocarbamate interactions (Scheme 1). The coordination chemistry of the dithiocarbamate ligand has been extensively documented,[8] but its application in the field of self-assembly has only recently been reported.[9] This is surprising, given the virtues of the dithiocarbamate motif. For example, dialkyldithiocarbamates form complexes with a wide variety of transition metals; this offers plenty of scope for introducing different metals into the supramolecular array. Secondly, the optical and electrochemical properties of dithiocarbamate complexes can be used to construct sensors for guest molecules.[9a,b] Thirdly, dithiocarbamates are known to stabilise unusually high oxidation states of metal ions.[10] This suggests that complex geometry could be manipulated by adjusting the metal oxidation state.

The ligand design reported here incorporates two dithiocarbamate anions suspended from an *m*-terphenyl scaffold, as depicted in Scheme 1. The *m*-terphenyl moiety was chosen because its relative rigidity preorganises the ligand for self-assembly. In addition, the preparation of *m*-terphenyl building blocks has been established in the literature and allows functional groups to be introduced at the Ar2′ position.[11] These substituents could be used to modify the cavity size or provide binding sites for inclusion of guest species. We describe here the synthetic approach to the dinuclear metallomacrocycles and the preliminary binding studies with Lewis basic guests.

Results and discussion

Syntheses

The synthesis of dinuclear macrocycles **5** and **6** is shown in Scheme 2. 4,4″-Bis(bromomethyl)-1,1′:3′,1″-terphenyl (**1**) and methyl-4,4″-bis(bromomethyl)-1,1′:3′,1″-terphenyl-2′-carboxylate (**2**) were prepared according to the multi-step sequence devised by Hart and Rajakumar.[11] Compounds **1** and **2** were then treated with excess n-butylamine to give diamine



Scheme 1 Metal-directed self-assembly of dinuclear macrocycles. Additional functional groups can be incorporated at the Ar2′ position (designated by X).

derivatives **3** and **4**, respectively, in quantitative yield. The ester functionalised diamine **4** was purified by conversion to the bis(hydrochloride) salt, followed by recrystallisation from MeOH–Et_2O. Diamine **3** could not be purified by this method, but was sufficiently pure to perform the subsequent step.

Addition of CS_2 to **3** and [**4**·2HCl] in alcoholic media gave the bis(dithiocarbamate) salts, which were coordinated to dipositive metal ions *in situ*. The resulting dinuclear macrocycles **5a**–**c** and **6a**–**b** were chromatographed on silica to afford the pure products in varying yields. Complexes **5a** and **5c** were assembled in good yield (72 and 67%, respectively), but the yields of **5b** and **6a**–**b** were considerably lower (20–44%). In particular, TLC showed the formation of nickel(II) complexes **5b** and **6b** was accompanied by several side products. It is not clear why the nature of the metal ion has such a significant effect on macrocycle yield.

Characterisation

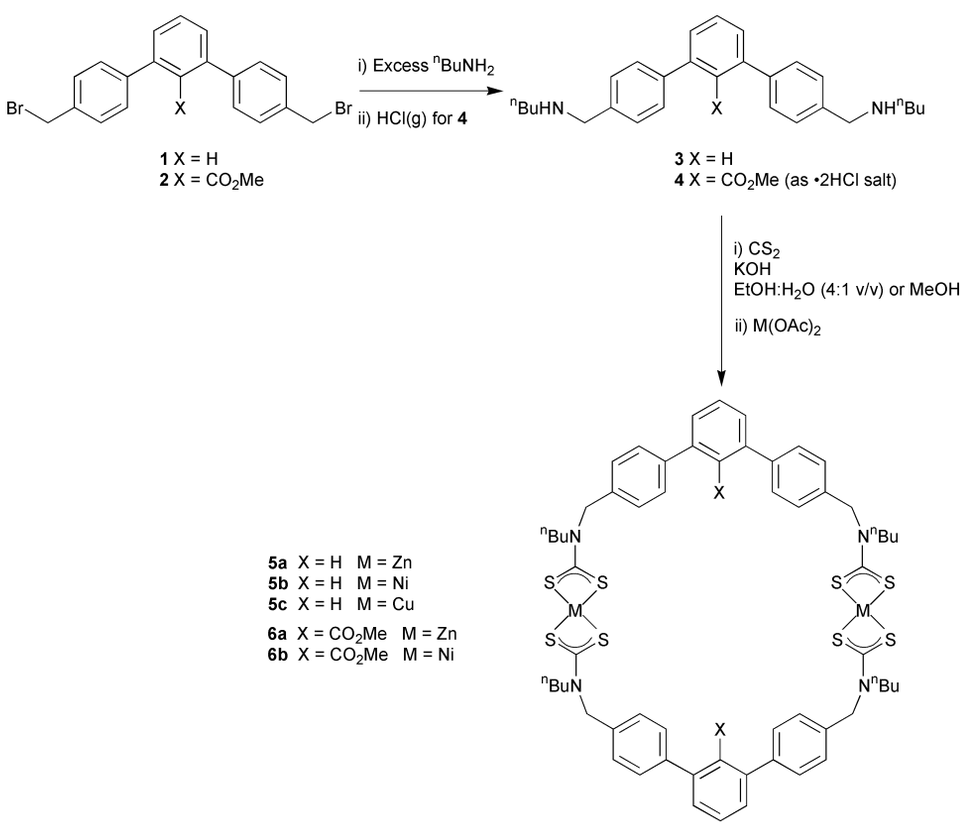
The dinuclear assemblies **5** and **6** were characterised by a variety of techniques, including ^{1}H NMR, ^{13}C NMR and UV-vis spectroscopy, cyclic voltammetry, elemental analysis and mass spectrometry. Fig. 1 illustrates the ^{1}H NMR spectrum of **5a**, which exemplifies typical features in the ^{1}H NMR of **5b** and **6a**–**b**. The copper(II) complex **5c** is paramagnetic and possesses only a broad, uninformative ^{1}H NMR spectrum. The ^{1}H NMR spectrum in Fig. 1 is relatively simple and is consistent with the symmetry of a dinuclear macrocyclic product. The set of resonances in the 7.4–7.8 ppm region is ascribed to the aromatic protons on the *m*-terphenyl ring (see Experimental section for full assignment). The ArCH_2N and NCH_2CH_2 signals are shifted markedly downfield ($\Delta\delta$ = 1.34 and 1.14 ppm, respectively) compared to the analogous protons on the parent diamine **3**. These protons are therefore diagnostic of dithiocarbamate formation. The high field region of the spectrum is characterised by three further resonances, which are readily assigned to the remaining $CH_2CH_2CH_3$ protons in the n-butyl chain.

The ^{13}C NMR spectra of **5a**–**b** and **6a**–**b** confirmed the presence of the CS_2 group at 205–208 ppm. The ester functionality in **6a**–**b** was observed at 170 ppm (C=O) and 52 ppm (OMe), while all four complexes displayed eight peaks for the eight magnetically distinct aromatic carbon atoms in the *m*-terphenyl ring. The five additional signals in the region from 14–57 ppm were assigned to the CH_2N^nBu moiety.

The electrospray mass spectrum of **5c** exhibited a base peak at *m*/*z* 1228 due to the molecular ion $[Cu(II)Cu(III)L_2]^+$ (Fig. 2). This species was generated by mono-oxidation of the dinuclear complex using the intrinsic electrochemical potential of the ESI source.[12] On oxidation with $NOBF_4$,[13] the doubly charged species $[Cu(III)Cu(III)L_2]^{2+}$ was observed at *m*/*z* 614, together with the tetrafluoroborate adduct $[Cu(III)Cu(III)L_2{\cdot}BF_4]^+$ at *m*/*z* 1315.

In contrast, no molecular ions (M^+) were observed in the ES mass spectra of zinc(II) and nickel(II) complexes **5**/**6a**–**b**. This is presumably due to the higher oxidation potentials of Zn(II) and Ni(II) dithiocarbamates relative to their Cu(II) counterparts.[10] However, all four complexes **5**/**6a**–**b** did give peaks corresponding to $[M + K]^+$ when the samples were coinjected with KPF_6. In addition, the nickel(II) complexes **5b** and **6b** showed clusters attributable to $[2M + K]^+$ and $[M + M/2 + K]^+$, respectively. These are probably due to multiple association of M and M/2 with potassium, rather than discrete tetrameric or trimeric macrocycles. This conclusion is supported by the fact that $Ni(et_2dtc)_2$ (et_2dtc = diethyldithiocarbamate) forms such species as $[2Ni(et_2dtc)_2 + Li]^+$ and $[Ni(et_2dtc)_2{\cdot}Ni(et_2dtc)]^+$ when the ES mass spectrum is recorded in the presence of lithium triflate.[12]

The UV-vis spectra of complexes **5** and **6** were recorded as 1×10^{-5} M solutions in CH_2Cl_2 and the results are presented in Table 1. The zinc(II) complexes **5**/**6a** both show one broad, dominant peak around 265 nm assigned to a ligand-centred (LC) π–π^* transition within the dithiocarbamate group.[14] Two shoulders were recorded for **6a** at 250 and 285 nm, but these were not resolved for the congener **5a**. No transitions were observed in the visible region for **5**/**6a**, consistent with the d^{10}



Scheme 2

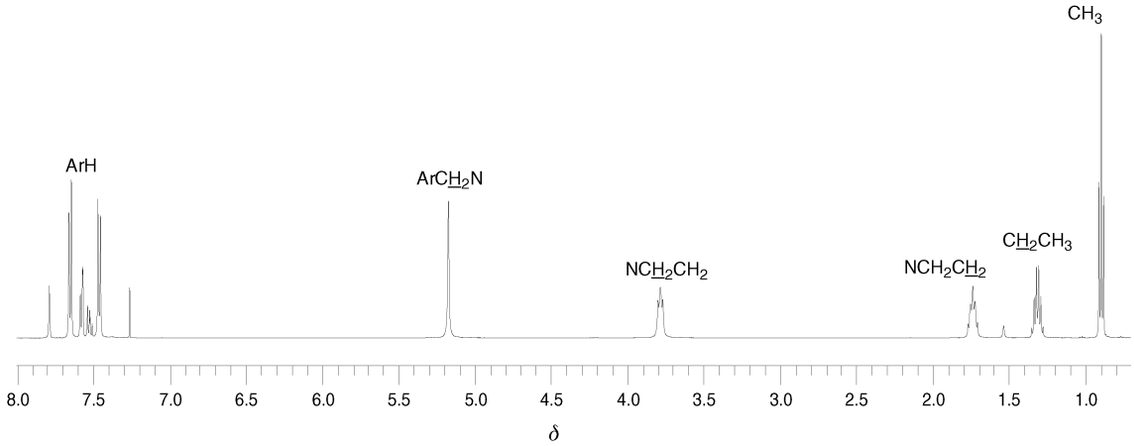


Fig. 1 ^{1}H NMR spectrum of complex **5a** (500 MHz, $CDCl_3$).

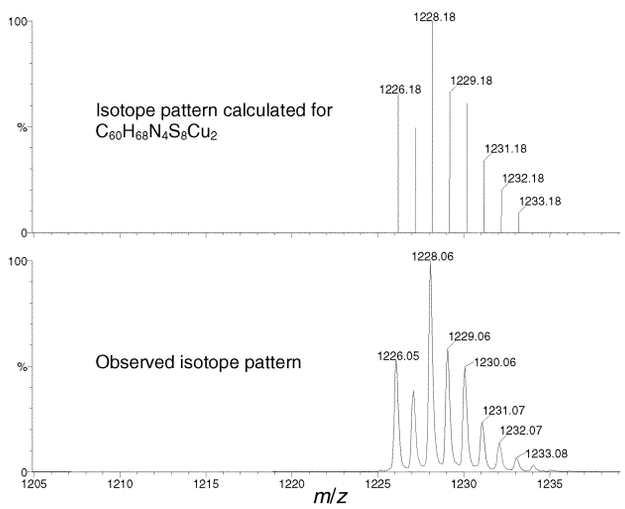


Fig. 2 Electrospray mass spectrum of complex **5c**, showing the theoretical and observed isotope patterns for the molecular ion $[\mathbf{5c}]^+$.

Table 1 UV-Vis spectroscopic data for complexes **5** and **6**[a]

Complex	λ/nm (ε/10^3 M^{-1} cm^{-1})
5a	267 (137.0)
5b	396 (10.5), 326 (75.9), 251 (115.8)
5c	437 (24.7), 272 (123.5), 245 sh (72.3)
6a	285 sh (47.6), 264 (101.3), 250 sh (8.70)
6b	397 (12.6), 326 (75.6), 248 (108.8)

[a] Recorded as 1×10^{-5} M solutions in CH_2Cl_2 at 298 K.

configuration of the Zn(II) ion.[15] In contrast, the nickel(II) complexes **5/6b** both exhibit two intense peaks in the UV region assigned to LC π–π* transitions[16] and a weaker, charge transfer band in the visible.[16,17] Low intensity, long wavelength d–d bands have been reported in the literature for nickel(II) dithiocarbamate systems,[16,17] but these were not discernible in the present case. The copper(II) macrocycle **5c** displays charge transfer transitions at 437 nm[18] and 245 nm,[14] in addition to a LC π–π* band[14] at 272 nm.

The copper(II) complex **5c** was further investigated by cyclic voltammetry in 4 : 1 CH_2Cl_2 : CH_3CN. A two-electron reversible oxidation wave was observed at 0.23 V. This wave is assigned to two identical Cu(II)/Cu(III) couples in the dinuclear complex. The simultaneous electron transfer confirms that the metals are too far apart to communicate electronically.[19]

Investigation of guest binding with hosts 5a and 6a

The self-assembly of complexes **5** and **6** generates macrocyclic cavities with the potential for guest inclusion. This possibility was explored with the zinc(II) assemblies **5/6a** and bidentate Lewis bases. It was postulated that suitably sized guests could bridge the two zinc(II) centres to form a cascade complex. Cascade coordination has been widely documented in the literature.[20] For example, Maverick *et al.* reported the self-assembly of dinuclear copper(II) macrocycles based on bis(β-diketone) ligands and demonstrated intramolecular binding of bidentate nitrogen bases.[21]

Nitrogen base adducts with zinc(II) dithiocarbamates have been detailed by several researchers.[15,22] For example, Ramalingam *et al.* have reported the X-ray crystal structures of dimeric $[Zn_2(deadtc)_4(4,4'\text{-bpy})]$ (deadtc = di(2-hydroxyethyl)dithiocarbamate) and $[Zn_2(nmedtc)_4(4,4'\text{-bpy})]$ (nmedtc = *N*-methyl-*N*-ethanoldithiocarbamate).[15] The two bis(dialkyldithiocarbamate)zinc(II) molecules are bridged by a 4,4′-bipyridyl linker in each case. Molecular models suggested that 4,4′-bipyridyl was suitably sized to span the two zinc(II) ions in complex **5a**.[23] A solution of **5a** in CH_2Cl_2 was therefore stirred with an equimolar quantity of 4,4′-bipyridyl overnight to afford a pale yellow precipitate **7**. The ^{1}H NMR spectrum of this product displayed several salient features (Fig. 3). The first point to note is the 1 : 1 ratio of **5a**: 4,4′-bipyridyl, determined by relative integration of the host and guest signals. This conclusion is supported by microanalytical data and is consistent with the 1 : 1 inclusion complex depicted in Fig. 3. Secondly, the guest protons in **7** show substantial downfield shifts relative to free 4,4′-bipyridyl ($\Delta\delta = +0.51$ and $+0.25$ ppm for py2 and py3, respectively). This is due to coordination of 4,4′-bipyridyl to both metal centres.[24] As anticipated, the py2 protons experience the largest change in chemical shift (Fig. 3); these protons are α to the coordinating nitrogen atoms. Thirdly, the $ArCH_2NCH_2$ resonances are significantly broadened in **7** compared to **5a**. This suggests that the rotational motion of the host is slowed by internal coordination of 4,4′-bipyridyl. A similar phenomenon has been reported by Harding *et al.*[25] They demonstrated that guest inclusion in a zinc(II) macrocycle slowed rotation of aryl rings in the host, resulting in broadened signals for the aryl protons.

The ^{13}C NMR spectrum of complex **7** was fully assigned using long- and short-range ^{1}H–^{13}C NMR correlation experiments. Three peaks at 149.93, 146.93 and 122.56 ppm were observed in addition to the ^{13}C signals of **5a**. These were assigned to the 4,4′-bipyridyl carbons C2, C4 and C3, respectively. The NOESY spectrum of **7** revealed intramolecular cross-peaks between the $ArCH_2NCH_2CH_2$ protons and the resonance at 7.44 ppm, confirming the assignment of ArH3,3″,5,5″ to the 7.44 ppm doublet. An *intermolecular* NOE signal was detected between ArH3,3″,5,5″ and py2. A molecular model of the inclusion complex **7** confirmed the close proximity of these protons.[23] In addition, the FAB mass spectrum of **7** displayed

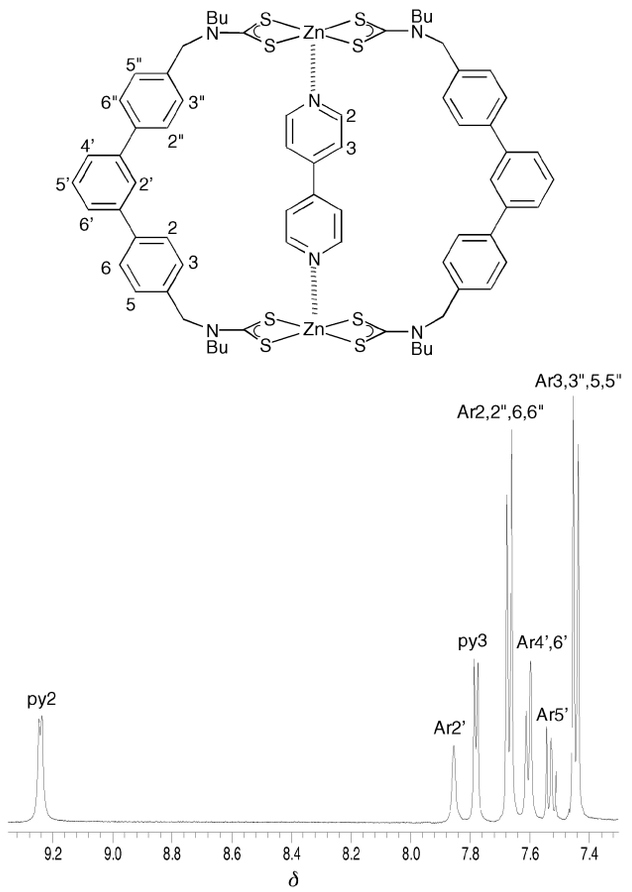


Fig. 3 ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of complex **7** formed from 4,4′-bipyridyl and **5a**.

two significant peaks at *m*/*z* 1232 and 1389. These were attributed to $[\mathbf{5a}]^+$ and the 1 : 1 complex $[\mathbf{5a}$ + 4,4′-bipyridyl$]^+$, respectively.

The interaction between **5a** and 4,4′-bipyridyl was explored further by performing a ^{1}H NMR titration in $CDCl_3$. The chemical shift of the py2 protons was monitored as a function of guest/host ratio and the resulting titration profile is presented in Fig. 4. As expected, the py2 chemical shifts at 10 : 1 and 1 : 1 ratios of guest : host are similar to the chemical shifts of free 4,4′-bipyridyl and complex **7**, respectively. However, the py2 signal moves further downfield at guest : host ratios < 1. This may reflect a deviation from the 1 : 1 complex stoichiometry at low concentrations of guest. For example, two hosts may associate with one guest when limited 4,4′-bipyridyl is present.

The reaction of 4,4′-bipyridyl with **6a** afforded the 1 : 1 adduct **8**, which was identified by FAB mass spectrometry at *m*/*z* 1505. The 4,4′-bipyridyl protons again showed significant downfield shifts relative to the free ligand ($\Delta\delta$ = +0.45 and +0.88 ppm for py2 and py3, respectively). The change in chemical shift for the py2 protons is similar on coordination to **5a** and **6a**. However, the py3 resonance in **8** is shifted +0.63 ppm downfield compared to **7**. This is probably due to the anisotropic field surrounding the carbonyl group in **8**, which affects the chemical shift of the proximate py3 protons.[26] The $ArCH_2NCH_2CH_2$ and CO_2Me proton signals are broad for adduct **8** at 293 K. In particular, the $ArCH_2NCH_2$ are severely broadened in comparison to **7** at this temperature. Interestingly, the $ArCH_2NCH_2CH_2$ and CO_2Me signals become less broad on heating **8** to 323 K. These results suggest that guest inclusion inhibits the rotational motion of the host (*vide supra*). Steric interactions between the ester and 4,4′-bipyridyl groups in **8** may explain why the $ArCH_2NCH_2$ signals are significantly broader in **8** relative to **7**.

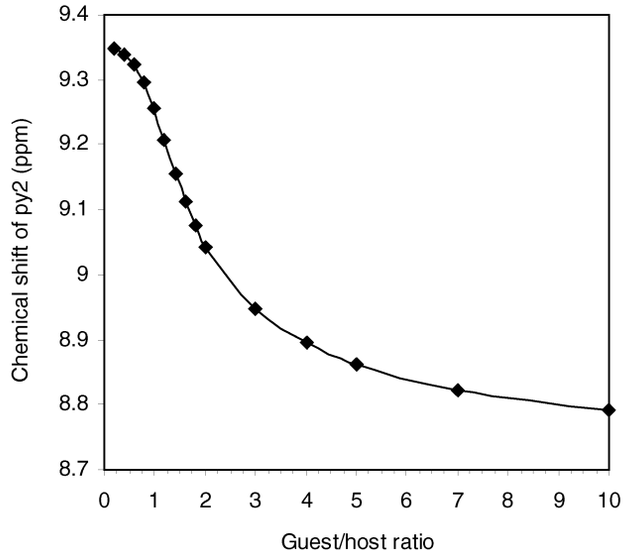


Fig. 4 Reverse sigmoidal plot for the titration of host **5a** with guest 4,4′-bipyridyl in $CDCl_3$.

Molecular models suggest that **5a** is sufficiently flexible to accommodate larger substrates such as 1,2-bis(4-pyridyl)-ethane.[23] This hypothesis was tested by stirring equimolar amounts of **5a** and 1,2-bis(4-pyridyl)ethane in $CHCl_3$ to afford complex **9**. Unfortunately, the FAB mass spectrum of **9** only displayed peaks attributable to the parent complex **5a**. However, the ^{1}H NMR spectrum of **9** clearly revealed a 1 : 1 adduct, with downfield perturbations of the bipyridyl protons on coordination to zinc(II). The presence of the guest was also identified in the ^{13}C NMR spectrum by peaks at 150.64 (py4), 149.56 (py2), 124.09 (py3) and 35.63 ($pyCH_2$). The positions of the remaining ^{13}C NMR signals were similar to those of **5a** in compound **7**.

Conclusion

The preparation of dithiocarbamate ligands based on an *m*-terphenyl framework has been described. These ligands self-assemble with transition metal cations to afford dinuclear metallomacrocycles in varied yields from 20–72%. The assemblies have been characterised by ^{1}H NMR, ^{13}C NMR and UV-vis spectroscopy, elemental analysis, mass spectrometry and cyclic voltammetry.

The zinc(II) complexes **5/6a** form 1 : 1 inclusion complexes with bidentate Lewis bases such as 4,4′-bipyridyl. Evidence for internal coordination was obtained from ^{1}H NMR and ^{13}C NMR spectroscopy, NOESY and ^{1}H–^{13}C NMR correlation experiments, FAB mass spectrometry and microanalytical data. The results demonstrate the potential of these systems to act as binuclear receptors for neutral guests.

Experimental

General

NMR spectra were recorded on Varian or Bruker 300 MHz and Varian 500 MHz spectrometers. Mass spectrometry was carried out at the SERC Mass Spectrometry Service, Swansea and the Inorganic Chemistry Laboratory, Oxford. Elemental analysis was performed at the Inorganic Chemistry Laboratory, Oxford. Electronic spectra were recorded on a Perkin-Elmer Lambda 6 UV-vis spectrometer. Electrochemical measurements were carried out using an EG & G Princeton Applied Research 362 scanning potentiostat. A three electrode system was employed with a platinum wire working electrode, an Ag/Ag^+ reference electrode and a platinum mesh counter electrode. Electrode potentials are quoted for 1 mM solutions in 4 : 1 CH_2Cl_2 :

CH_3CN (in the presence of 0.1 M $TBABF_4$ as supporting electrolyte), at 100 mV s^{-1} scan rate.

4,4″-Bis(bromomethyl)-1,1′:3′,1″-terphenyl (**1**) and methyl-4,4″-bis(bromomethyl)-1,1′:3′,1″-terphenyl-2′-carboxylate (**2**) were synthesised according to a literature procedure.[11]

Syntheses

Ligand 3. 4,4″-Bis(bromomethyl)-1,1′:3′,1″-terphenyl (**1**) (1.38 g, 3.32 mmol) was added portionwise over 10 min to n-butylamine (30 mL, excess) and the mixture stirred for 1.5 h. CH_2Cl_2 (80 mL) was added and the organic solution was washed with H_2O (4 × 50 mL), dried ($MgSO_4$) and then evaporated to afford the product as a colourless oil (1.33 g, quantitative yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (1H, t, J = 1.8 Hz, ArH2′), 7.62 (4H, d, J = 8 Hz, ArH2,2″,6,6″), 7.57 (2H, m, ArH4′,6′), 7.50 (1H, m, ArH5′), 7.42 (4H, d, J = 8 Hz, ArH3,3″,5,5″), 3.83 (4H, s, $ArCH_2$), 2.64 (4H, t, J = 7.3 Hz, NCH_2CH_2), 1.49 (4H, quint, J = 7.4 Hz, NCH_2CH_2), 1.34 (6H, m, CH_2CH_3, NH), 0.89 (6H, t, J = 7.3 Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 141.51, 139.83, 139.73, 129.09, 128.51, 127.16, 125.86, 53.73 ($ArCH_2$), 49.21 (NCH_2CH_2), 32.24 (NCH_2CH_2), 20.46 (CH_2CH_3), 13.99 (CH_3). (Found: C, 80.9; H, 9.1; N, 6.8. $C_{28}H_{36}N_2 \cdot H_2O$ requires C, 80.3; H, 9.2; N, 6.7%.) FAB-MS: m/z 401 $(M + H)^+$, 326 $(M - NHC_4H_9 - 2H)^+$, 256 $(M - 2NHC_4H_9)^+$.

Ligand 4. Preparation as for ligand **3** using methyl-4,4″-bis-(bromomethyl)-1,1′:3′,1″-terphenyl-2′-carboxylate (**2**) (1.06 g, 2.24 mmol) and n-butylamine (15 mL, excess). This gave the crude amine as a yellow oil (1.01 g, 99%). Ligand **4** was purified by bubbling HCl(g) through a solution of the amine in $CHCl_3$ (50 mL) to yield the bis(HCl) salt as a white precipitate. This was collected by filtration and recrystallised from MeOH–Et_2O to give the product as a white solid (0.762 g, 64%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.19 (4H, s, br, NH_2^+), 7.64 (5H, m, ArH), 7.43 (6H, m, ArH), 4.16 (4H, m, br, $ArCH_2$), 2.89 (4H, m, NCH_2CH_2), 1.64 (4H, quint, J = 7.6 Hz, NCH_2CH_2), 1.33 (4H, sext, J = 7.3 Hz, CH_2CH_3), 0.88 (6H, t, J = 7.2 Hz, CH_2CH_3). (CO_2Me singlet coincident with water at *ca.* 3.3 ppm.) ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 169.07 (C=O), 140.39, 139.16, 132.27, 131.77, 130.35, 130.19, 129.23, 128.35, 51.91, 49.58, 46.38, 27.40, 19.51, 13.61. (Found: C, 67.2; H, 7.9; N, 5.1. $C_{30}H_{40}N_2O_2Cl_2$ requires C, 67.8; H, 7.6; N, 5.3%.) ES-MS: m/z 459 $(M - 2HCl)^+$, 386 $(M - 2HCl - NHC_4H_9)^+$, 345 $(M - 2Cl - H - 2C_4H_9)^+$, 330 $(M - HCl - 2C_4H_9 - NH)^+$, 315 $(M - 2ClNH_2C_4H_9 + H)^+$.

Complex 5a. Ligand **3** (0.500 g, 1.25 mmol) in MeOH (35 mL) was treated with KOH(aq) (1.57 M, 3.2 mL) followed by CS_2 (0.30 mL, 4.99 mmol) and the mixture stirred for 0.5 h. Zinc(II) acetate dihydrate (0.301 g, 1.37 mmol) in H_2O (3 mL) was then added dropwise and the mixture stirred for 15 h. The precipitate was removed by filtration, washed with MeOH (30 mL) and dried under vacuum. The crude product was chromatographed on silica with CH_2Cl_2 and the product band concentrated to 20 mL. This solution was added dropwise to MeOH (150 mL) to give a white precipitate, which was removed by filtration and dried under vacuum (0.551 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (2H, s, ArH2′), 7.65 (8H, d, J = 8.5 Hz, ArH2,2″,6,6″), 7.58 (4H, m, ArH4′,6′), 7.52 (2H, m, ArH5′), 7.46 (8H, d, J = 8 Hz, ArH3,3″,5,5″), 5.17 (8H, s, $ArCH_2$), 3.78 (8H, t, J = 7.5 Hz, NCH_2CH_2), 1.74 (8H, quint, J = 7.8 Hz, NCH_2CH_2), 1.31 (8H, sext, J = 7.5 Hz, CH_2CH_3), 0.89 (12H, t, J = 7.3 Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 204.62 (CS_2), 141.15, 140.89, 134.03, 129.31, 128.26, 127.65, 126.20, 125.98, 57.14 ($ArCH_2$), 53.60 (NCH_2CH_2), 28.62 (NCH_2CH_2), 19.99 (CH_2CH_3), 13.69 (CH_3). (Found: C, 58.4; H, 5.2; N, 4.4. $C_{60}H_{68}N_4S_8Zn_2$ requires C, 58.5; H, 5.6; N, 4.6%.) ES-MS (+KPF_6): m/z 1270 $(M + K)^+$.

Complex 5b. Preparation as for **5a**, using ligand **3** (0.300 g, 0.749 mmol), KOH(aq) (0.80 M, 1.9 mL), CS_2 (0.18 mL, 3.00 mmol), nickel(II) acetate tetrahydrate (0.186 g, 0.749 mmol) and CH_2Cl_2–hexane (2 : 1 v/v) eluent. The product was obtained as a green solid (0.166 g, 36%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.06 (2H, s, br, ArH2′), 7.89 (8H, d, J = 6.5 Hz, ArH2,2″,6,6″), 7.73 (4H, d, J = 7.5 Hz, ArH4′,6′), 7.60 (2H, t, J = 7.8 Hz, ArH5′), 7.46 (8H, d, J = 7.5 Hz, ArH3,3″,5,5″), 4.90 (8H, s, br, $ArCH_2$), 3.53 (8H, s, br, NCH_2CH_2), 1.58 (8H, m, NCH_2CH_2), 1.25 (8H, m, CH_2CH_3), 0.85 (12H, t, J = 7.3 Hz, CH_3). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 205.42 (CS_2), 140.13, 139.60, 134.17, 129.77, 128.50, 127.30, 125.98, 124.89, 51.44 ($ArCH_2$), 49.00 (NCH_2CH_2), 28.67 (NCH_2CH_2), 19.62 (CH_2CH_3), 13.82 (CH_3). (Found: C, 59.1; H, 5.6; N, 4.4. $C_{60}H_{68}N_4S_8Ni_2$ requires C, 59.1; H, 5.6; N, 4.6%.) ES-MS (+KPF_6): m/z 2475 $(2M + K)^+$, 1257 $(M + K)^+$, 608 $(M/2)^+$.

Complex 5c. Preparation as for **5a**, using ligand **3** (0.463 g, 1.16 mmol), KOH(aq) (1.31 M, 3.5 mL), CS_2 (0.28 mL, 4.62 mmol), copper(II) acetate hydrate (0.254 g, 1.27 mmol) and $CHCl_3$ eluent. The product was obtained as a brown solid (0.476 g, 67%). (Found: C, 57.8; H, 5.6; N, 4.6. $C_{60}H_{68}N_4S_8Cu_2 \cdot H_2O$ requires C, 57.8; H, 5.7; N, 4.5%.) ES-MS: m/z 1228 (M^+).

Complex 6a. Ligand **4** (0.250 g, 0.470 mmol) in EtOH–H_2O (4 : 1 v/v, 15 mL) was treated with KOH(aq) (0.63 M, 3 mL) followed by CS_2 (0.06 mL, 0.988 mmol) and the mixture stirred for 20 min. Zinc(II) acetate dihydrate (0.114 g, 0.517 mmol) in H_2O (10 mL) was then added dropwise and the mixture stirred for 1 h. The precipitate was removed by filtration, suspended in Et_2O (75 mL), stirred for 15 min and re-filtered. The residue was purified by column chromatography on silica with $CHCl_3$–EtOAc (20 : 1 v/v). The product band was concentrated to 10 mL and added dropwise to MeOH (75 mL) to yield a white precipitate. This was collected by filtration and dried under vacuum to afford the product as a white solid (0.138 g, 44%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (2H, t, J = 8 Hz, ArH5′), 7.39 (20H, m, ArH), 5.14 (8H, s, $ArCH_2$), 3.76 (8H, m, NCH_2CH_2), 3.37 (6H, s, CO_2Me), 1.71 (8H, quint, br, NCH_2CH_2), 1.31 (8H, sext, J = 7.5 Hz, CH_2CH_3), 0.89 (12H, t, J = 7.5 Hz, CH_2CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 204.46 (CS_2), 169.65 (C=O), 140.22, 139.69, 134.11, 132.60, 129.50, 128.94, 128.78, 127.75, 57.15 ($ArCH_2$), 53.57 (NCH_2CH_2), 51.91 (CO_2Me), 28.56 (NCH_2CH_2), 19.96 (CH_2CH_3), 13.67 (CH_2CH_3). (Found: C, 57.2; H, 5.6; N, 4.1. $C_{64}H_{72}N_4O_4S_8Zn_2$ requires C, 57.0; H, 5.4; N, 4.2%.) ES-MS (+KPF_6): m/z 1387 $(M + K)^+$, 1371 $(M + Na)^+$.

Complex 6b. Preparation as for **6a**, using ligand **4** (0.117 g, 0.221 mmol), KOH(aq) (0.37 M, 2.4 mL), CS_2 (0.03 mL, 0.464 mmol), nickel(II) acetate tetrahydrate (0.060 g, 0.243 mmol) and $CHCl_3$–EtOAc (40 : 1 v/v) eluent. The product was obtained as a green solid (0.029 g, 20%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (2H, t, J = 8 Hz, ArH5′), 7.32–7.44 (20H, m, ArH), 4.81 (8H, s, $ArCH_2$), 3.48 (8H, m, NCH_2CH_2), 3.37 (6H, s, CO_2Me), 1.56 (8H, m, NCH_2CH_2), 1.27 (8H, sext, J = 7.5 Hz, CH_2CH_3), 0.86 (12H, t, J = 7.5 Hz, CH_2CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 208.05 (CS_2), 169.63 (C=O), 140.41, 139.63, 133.60, 132.60, 129.57, 129.02, 128.84, 128.16, 51.94 (CO_2Me), 51.51 ($ArCH_2$), 48.40 (NCH_2CH_2), 28.81 (NCH_2CH_2), 19.92 (CH_2CH_3), 13.67 (CH_2CH_3). (Found: C, 57.2; H, 5.6; N, 4.2. $C_{64}H_{72}N_4O_4S_8Ni_2$ requires C, 57.6; H, 5.4; N, 4.2%.) ES-MS (+KPF_6): m/z 2042 $(M + M/2 + K)^+$, 2026 $(M + M/2 + Na)^+$, 1373 $(M + K)^+$, 1357 $(M + Na)^+$.

Complex 7. A solution of 4,4′-bipyridyl (11.3 mg, 72.4 μmol) in CH_2Cl_2 (5 mL) was added to a solution of **5a** (89.3 mg, 72.4 μmol) in CH_2Cl_2 (5 mL) and the mixture was stirred for 15 h. The precipitate was removed by filtration and washed

with CH_2Cl_2 (5 mL) to give complex **7** as a pale yellow solid (91.3 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.24 (4H, d, J = 5.5 Hz, py2), 7.85 (2H, s, ArH2′), 7.78 (4H, d, J = 6 Hz, py3), 7.67 (8H, d, J = 8 Hz, ArH2,2″,6,6″), 7.60 (4H, d, J = 7 Hz, ArH4′,6′), 7.53 (2H, m, ArH5′), 7.44 (8H, d, J = 8.5 Hz, ArH3,3″,5,5″), 5.24 (8H, s, br, $ArCH_2$), 3.87 (8H, s, br, NCH_2CH_2), 1.80 (8H, quint, J = 7.3 Hz, NCH_2CH_2), 1.35 (8H, sext, J = 7.4 Hz, CH_2CH_3), 0.92 (12H, t, J = 7.3 Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 205.97 (CS_2), 149.93 (py2), 146.93 (py4), 140.82 (ArC1′,3′), 140.06 (ArC1,1″), 135.02 (ArC4,4″), 129.27 (ArC5′), 127.63 (ArC3,3″,5,5″), 127.20 (ArC2,2″,6,6″), 126.06 (ArC4′,6′), 125.12 (ArC2′) 122.56 (py3), 57.14 ($ArCH_2$), 54.28 (NCH_2CH_2), 28.92 (NCH_2CH_2), 20.18 (CH_2CH_3), 13.90 (CH_3). (Found: C, 59.8; H, 5.8; N, 5.7. $C_{70}H_{76}N_6S_8Zn_2\cdot H_2O$ requires C, 59.8; H, 5.6; N, 6.0%.) FAB-MS: *m*/*z* 1389 $(M)^+$, 1232 $(M - C_{10}H_8N_2)^+$.

Complex 8. A solution of 4,4′-bipyridyl (4.9 mg, 31.6 μmol) in CH_2Cl_2 (2 mL) was added to a solution of **6a** (42.6 mg, 31.6 μmol) in CH_2Cl_2 (4 mL) and the mixture was stirred for 21 h. The yellow solution was added dropwise to hexane to yield a precipitate, which was removed by filtration. The pale yellow solid was dried under vacuum (25.0 mg, 53%). ^{1}H NMR at 50 °C (500 MHz, $CDCl_3$): δ 9.16 (4H, d, J = 5.5 Hz, py2), 8.29 (4H, d, J = 4 Hz, py3), 7.53 (10H, m, ArH), 7.44 (8H, d, J = 7.5 Hz, ArH), 7.40 (4H, d, J = 7.5 Hz, ArH), 5.23 (8H, s, br, $ArCH_2$), 3.98 (8H, s, br, NCH_2CH_2), 3.17 (6H, s, CO_2Me), 1.82 (8H, m, NCH_2CH_2), 1.39 (8H, m, CH_2CH_3), 0.94 (12H, t, J = 7.3 Hz, CH_2CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.71 (CS_2), 170.25 (C=O), 150.04 (py2), 146.01 (py4), 139.92, 139.22, 135.74, 132.14, 129.59, 128.96, 126.50, 122.40 (py3), 57.35 ($ArCH_2$), 55.88 (NCH_2CH_2), 52.45 (CO_2Me), 29.44 (NCH_2CH_2), 20.24 (CH_2CH_3), 13.94 (CH_2CH_3). (Found: C, 58.9; H, 5.1; N, 5.6. $C_{74}H_{80}N_6O_4S_8Zn_2$ requires C, 59.1; H, 5.4; N, 5.6%.) FAB-MS: *m*/*z* 1505 $(M)^+$, 1346 $(M - C_{10}H_{10}N_2)^+$.

Complex 9. A solution of 1,2-bis(4-pyridyl)ethane (0.023 g, 0.123 mmol) in $CHCl_3$ (10 mL) was added dropwise to a solution of **5a** (0.152 g, 0.123 mmol) in $CHCl_3$ (35 mL). The mixture was stirred for 15 h, filtered and the filtrate added dropwise to hexane (100 mL) to yield a white precipitate. This was collected by filtration and dried under vacuum to give the product as a grey solid (0.129 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (4H, d, J = 5.5 Hz, py2), 7.80 (2H, s, ArH2′), 7.64 (8H, d, J = 8 Hz, ArH2,2″,6,6″), 7.58 (4H, d, J = 7.5 Hz, ArH4′,6′), 7.52 (2H, m, ArH5′), 7.46 (8H, d, J = 8 Hz, ArH3,3″,5,5″), 7.17 (4H, d, J = 5.5 Hz, py3), 5.18 (8H, s, br, $ArCH_2$), 3.81 (8H, m, NCH_2CH_2), 2.97 (4H, s, $pyCH_2$), 1.76 (8H, quint, J = 7.5 Hz, NCH_2CH_2), 1.32 (8H, sext, J = 7.5 Hz, CH_2CH_3), 0.90 (12H, t, J = 7.5 Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 205.64 (CS_2), 150.64 (py4), 149.56 (py2), 141.14 (ArC1′,3′), 140.42 (ArC1,1″), 134.74 (ArC4,4″), 129.20 (ArC5′), 127.97 (ArC3,3″,5,5″), 127.42 (ArC2,2″,6,6″), 126.00 (ArC2′,4′,6′) 124.09 (py3), 57.26 ($ArCH_2$), 54.07 (NCH_2CH_2), 35.63 ($pyCH_2$), 28.77 (NCH_2CH_2), 20.19 (CH_2CH_3), 13.89 (CH_3). (Found: C, 60.8; H, 5.2; N, 5.9. $C_{72}H_{80}N_6S_8Zn_2$ requires C, 61.0; H, 5.7; N, 5.9%.) FAB-MS: *m*/*z* 1231 $(M - C_{12}H_{12}N_2)^+$.

Acknowledgements

We gratefully acknowledge the Leverhulme Trust for a post-doctoral fellowship (L. H. U. and J. M. W.). We thank Dr Nick Rees for performing the NOESY experiment and the EPSRC for use of the mass spectrometry service at the University of Wales, Swansea.

References

1 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995, ch. 9; B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185; B. Linton and A. D. Hamilton, *Chem. Rev.*, 1997, **97**, 1669; M. Fujita and K. Ogura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1471.

2 D. L. Caulder and K. N. Raymond, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1440; R. M. Yeh, M. Zeigler, D. W. Johnson, A. J. Terpin and K. N. Raymond, *Inorg. Chem.*, 2001, **40**, 2216; D. A. McMorran and P. J. Steel, *Angew. Chem., Int. Ed.*, 1998, **37**, 3295; R. Krämer, J.-M. Lehn, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703; B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1838; F. M. Tabellion, S. R. Seidel, A. M. Aril and P. J. Stang, *Angew. Chem., Int. Ed.*, 2001, **40**, 1529.

3 J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffrey, J. A. McCleverty and M. D. Ward, *Angew. Chem., Int. Ed.*, 1998, **37**, 1279; T. Beissel, R. E. Powers and K. N. Raymond, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1084; M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 1649; R. Vilao, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Angew. Chem. Int., Ed.*, 1998, **37**, 1258; S.-S. Sun and A. J. Lees, *Chem. Commun.*, 2001, 103; P. N. W. Baxter, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1999, **5**, 102.

4 (*a*) W. Huang, S. Gou, D. Hu, S. Chantrapromma, H.-K. Fun and Q. Meng, *Inorg. Chem.*, 2001, **40**, 1712; (*b*) P. N. W. Baxter, G. S. Hanan and J.-M. Lehn, *Chem. Commun.*, 1996, 2019.

5 P. Ceroni, A. Credi, V. Balzani, S. Campagna, G. S. Hanan, C. R. Arana and J.-M. Lehn, *Eur. J. Inorg. Chem.*, 1999, 1409; G. S. Hanan, C. R. Arana, J.-M. Lehn and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1122.

6 M.-T. Youinou, N. Rahmouni, J. Fischer and J. A. Osborn, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 733; J. Rojo, F. J. Romero-Salguero, J.-M. Lehn, G. Baum and D. Fenske, *Eur. J. Inorg. Chem.*, 1999, 1421; P. N. W. Baxter, J.-M. Lehn, J. Fischer and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2284; E. Breuning, U. Ziener, J.-M. Lehn, E. Wegelius and K. Rissanen, *Eur. J. Inorg. Chem.*, 2001, 1515.

7 J. S. Lindsey, *New J. Chem.*, 1991, **15**, 153.

8 D. J. Halls, *Mikrochim. Acta*, 1969, 62; D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11**, 233; D. Coucouvanis, *Prog. Inorg. Chem.*, 1979, **26**, 301.

9 (*a*) P. D. Beer, N. Berry, M. G. B. Drew, O. D. Fox, M. E. Padilla-Tosta and S. Patell, *Chem. Commun.*, 2001, 199; (*b*) O. D. Fox, M. G. B. Drew, E. J. S. Wilkinson and P. D. Beer, *Chem. Commun.*, 2000, 391; (*c*) O. D. Fox, M. G. B. Drew and P. D. Beer, *Angew. Chem., Int. Ed.*, 2000, **39**, 136.

10 R. Chant, A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Aust. J. Chem.*, 1973, **26**, 2533.

11 H. Hart and P. Rajakumar, *Tetrahedron*, 1995, **51**, 1313.

12 D. F. Schoener, M. A. Olsen, P. G. Cummings and C. Basic, *J. Mass Spectrom.*, 1999, **34**, 1069.

13 A. M. Bond, R. Colton, A. D'Agostino, J. Harvey and J. C. Traeger, *Inorg. Chem.*, 1993, **32**, 3952.

14 D. Oktavec, J. Štefanec, B. Síleš, E. Beinrohr, V. Konečný and J. Garaj, *Collect. Czech. Chem. Commun.*, 1982, **47**, 2867.

15 A. Manohar, K. Ramalingam, G. Bocelli and L. Righi, *Inorg. Chim. Acta*, 2001, **314**, 177.

16 M. Castillo, J. J. Criado, B. Macias and M. V. Vaquero, *Inorg. Chim. Acta*, 1986, **124**, 127; M. Castillo, J. J. Criado, B. Macias and M. V. Vaquero, *Transition Met. Chem.*, 1986, **11**, 476.

17 R. Dingle, *Inorg. Chem.*, 1971, **10**, 1141.

18 B. G. Jeliazkova and M. A. Doicheva, *Polyhedron*, 1996, **15**, 1277.

19 S.-S. Sun and A. J. Lees, *Inorg. Chem.*, 2001, **40**, 3154.

20 J.-M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441; P. D. Beer and D. K. Smith, *Prog. Inorg. Chem.*, 1997, **46**, 1; M. W. Gobel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1141.

21 A. W. Maverick and F. E. Klavetter, *Inorg. Chem.*, 1984, **23**, 4129; A. W. Maverick, S. C. Buckingham, Q. Yao, J. R. Bradbury and G. G. Stanley, *J. Am. Chem. Soc.*, 1986, **108**, 7430; A. W. Maverick, M. L. Ivie, J. H. Waggenspack and F. R. Fronczek, *Inorg. Chem.*, 1990, **29**, 2403.

22 M. A. Malik, M. Motevalli, P. O'Brien and J. R. Walsh, *Inorg. Chem.*, 1997, **36**, 1263.

23 CaChe 3.2 molecular modelling program, Oxford Molecular Group, Inc., 1999.

24 P. J. Stang, D. H. Cao, S. Saito and A. M. Arif, *J. Am. Chem. Soc.*, 1995, **117**, 6273.

25 A. Bilyk and M. M. Harding, *J. Chem. Soc., Chem. Commun.*, 1995, 1697; M. A. Houghton, A. Bilyk, M. M. Harding, P. Turner and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1997, 2725.

26 D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, 4th edn., 1989.