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Doubly-linked 1D coordination polymers derived from 2 : 2 metallamacrocyclic Ni(II) complexes with bipodal acylthiourea and *exo*-bidentate *N*-donor bridging ligands: toward potentially selective chemical sensors?†

Oren Hallale,[a] **Susan A. Bourne***[a] **and Klaus R. Koch***[b]

[a] *Department of Chemistry, University of Cape Town, Rondebosch, 7701, South Africa.*
E-mail: xraysue@science.uct.ac.za; Fax: (+27) 21 689 7499; Tel: (+27) 21 650 2653
[b] *Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland, 7602,*
South Africa. E-mail: krk@sun.ac.za; Fax: (+27) 21 808 3360; Tel: (+27) 21 808 3020

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The square planar 2 : 2 metallamacrocyclic Ni(II) complex of 3,3,3′,3′-tetraethyl-1,1′-isophthaloylbis(thiourea) readily forms coordination polymers by axial coordination of various *exo*-bidentate *N*-donor linkers: pyrazine, 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane and 1,2-di(4-pyridyl)ethylene. Steric constraints, together with coordination limited to the axial directions, result in the self-assembly of double-linked 1D ladder structures. One compound in particular, with the bridging ligand 1,2-di(4-pyridyl)ethylene, is found to exist as a quasi-polymer, realising only one-third of its potential linkages. On exposure to various solvents, this compound appears to undergo complete polymerisation, both rapidly and fully reversibly with an associated colour change, making it a potential chemical sensor.

Introduction

Our studies of bipodal 3,3,3′,3′-tetraalkyl-1,1′-phenylenedicarbonylbis(thiourea) compounds have revealed that they can act as pre-programmed chelating ligands to form d^8 square planar metallamacrocyclic complexes *via* self-assembly.[1–3] Metal-to-ligand stoichiometries of 2 : 2 or 3 : 3 are dictated by the use of *meta*- or *para*-substituted ligands, respectively (Fig. 1). Similar discrete metallamacrocyclic complexes have been synthesised by the use of other systems, for example the self-assembled complexes reported by Stang,[4] Aoyagi,[5] Matthews,[6] Rojo,[7] Soldatov,[8] and Song.[9]

We have also shown that octahedral adducts of both 2 : 2 and 3 : 3 Ni(II) metallamacrocycles can be obtained by the addition of pyridines.[2,3,10] Furthermore, the use of a bipodal ligand with hydroxyethyl side branches results in a 2 : 2 metallamacrocycle which, upon addition of pyridine, acts as a secondary building unit in the self-assembly of a complex 3D supramolecular framework. Similar applications have been reported by Moon,[11] Yaghi[12] and Zaworotko[13] for their discrete assemblies.

A logical direction for the development of the aroylbis(thioureato) metallamacrocycles is the axial coordination of *exo*-bidentate bridging ligands to the Ni(II) centres to act as linkers between complexes, thus assembling coordination polymers of metallamacrocycles. Many examples of such polymers are known, the most common bridging ligands used in coordination polymerisation are 4,4′-bipyridine (bipy)[14] and pyrazine (pyra).[15] The former has been referred to as "the classical molecular rod in constructing supramolecular polymetallic architectures".[16] While pyra and bipy are rigid *exo*-bidentate ligands, flexible analogues may be of use as well. 1,2-bis(4-pyridyl)ethane (BPE) is commonly used for this purpose.[17] These three ligands as well as a fourth, 1,2-di(4-pyridyl)ethylene (DPE), were selected as potential bridging linkers for transforming metallamacrocycles into polymeric arrays. The simpler 2 : 2 metallamacrocyclic complexes were chosen for initial study.

Since the 2 : 2 metallamacrocyclic complexes possess two available axial coordination sites per nickel atom, these compounds could be expected to act as 4-connected nodes for the purpose of assembly into polymeric arrays. However, molecular models indicate that two factors limit the manner in which these complexes may link up. Firstly, metal centres in successive metallamacrocycles must align themselves in a linear fashion as a result of the parallel directionality (orthogonal to the metallamacrocyclic plane) of the available coordination sites on the nickel atoms. Secondly, steric constraints prevent the close lateral alignment of two metallamacrocycles in any orientation. This can be seen by analysing the space filling representation of the metallamacrocycle *cis*-[Ni(I-Et-*S*,*O*)]$_2$ (Fig. 2), based on its crystal structure.[3] As a result of this spatial restriction, a metallamacrocycle cannot have another two such molecules approaching the same face and linking to each of its Ni(II) centres simultaneously. This limitation could possibly be overcome by the use of bridging ligands with longer, more flexible spacer groups.

If such lateral alignment was possible, the metallamacrocycles would possess true 4-connectivity and various 1D and 2D arrays would be possible, as shown in Fig. 3. Since this is not the case, the multiple connectivity of the 2 : 2 complexes is limited, and should be regarded as a double 2-connection rather than a 4-connection. Hence, these complexes are expected to form only linear coordination polymers, in which each 2 : 2 complex is doubly-connected to neighbouring complexes directly above and below the metallamacrocyclic plane. In other words, each metallamacrocycle could be viewed as a rung in a "supramolecular ladder".

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† Electronic supplementary information (ESI) available: TGA plots and HSM photographs of **2**–**5**; digital photographs and gravimetric studies of **5**. See http://dx.doi.org/10.1039/b509727d

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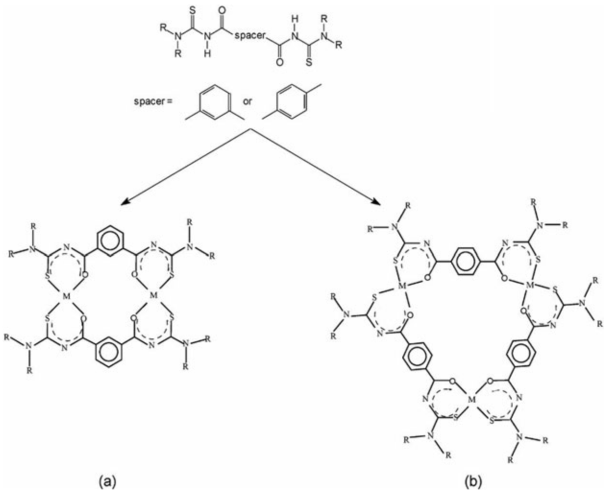

Fig. 1 Reaction scheme for the self-assembly of 2 : 2 and 3 : 3 metallamacrocyclic complexes with *meta*- and *para*-substituted 3,3,3′,3′-tetraalkyl-1,1′-phenylenedicarbonylbis(thiourea) ligands.

Because the bridging ligands in polymers of the predicted type would be shared between neighbouring metallamacrocycles (with the exception of terminal ligands), and since each metallamacrocycle would coordinate to four bridging ligands, it can be shown that the metallamacrocycle to bridging ligand ratio (MM : BL) should tend to 1 : 2, if the polymer chain length is long enough that the presence of unshared terminal ligands is negligible.

Since molecules of both solvents and uncoordinated ligands have been identified as guests in the octahedral adducts of 2 : 2 metallamacrocycles,[2,10] both types of compound are candidates for guests in the structures of coordination polymers. It is therefore convenient to also speak of ratios of metallamacrocycle, bidentate *N*-donor molecule (either as ligand or guest) and solvent molecule, or M : B : S.

There is much interest in vapochromic d^8 metal complexes because of their potential application as chemical sensors.[18] Similar properties have also been observed in coordination polymers involving other metals such as platinum,[19] copper,[20] and gold/thallium.[21] The mechanisms for the vapochromic phenomena are varied, but all seem to involve very slight disruptions to the crystal structure of the complex by the admission of solvent molecules bringing about a major change to their physical properties.

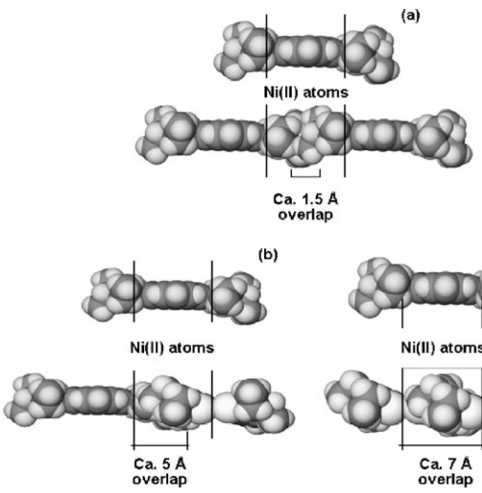

Fig. 2 Lateral approach of two 2 : 2 metallamacrocycles such that their Ni(II) centres will simultaneously link to the metal centres of a third such molecule. All of the (a) side-to-side, (b) head-to-side or (c) head-to-head orientations suffer from steric hindrance, preventing assembly based on these orientations.

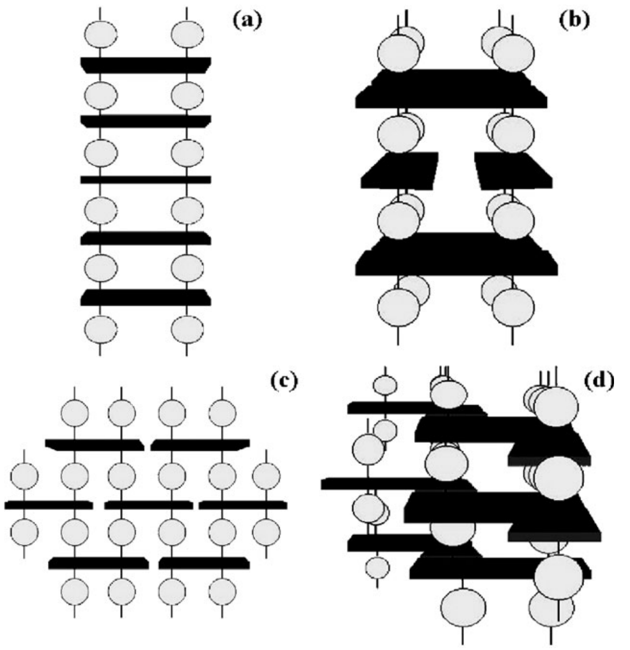

Fig. 3 Possible polymeric products of 2 : 2 metallamacrocycles: (a) a doubly-linked 1D "ladder" polymer, (b) a more complex 1D assembly with each level consisting of pairs of metallamacrocycles in alternating orientations, (c) a 2D "brick wall" array and (d) an undulating 2D array. Note: (b)–(d) require metallamacrocycles to possess true 4-connectivity and thus are precluded. Only (a), based on double 2-connections, is a possible product.

In this paper we report on a systematic investigation of some coordination polymers derived from the previously well characterized[2,3] 2 : 2 *cis*-[Ni(I-Et-*S*,*O*)]$_2$ complexes together with pyra, bipy, BPE and DPE respectively, the latter complex of which shows interesting solvatochromic behaviour.

Experimental

Preparative methods

3,3,3′,3′-Tetraethyl-1,1′-isophthaloylbis(thiourea) (H$_2$-I-Et). This ligand was synthesised according to the method of Douglass and Dains.[22] Isophthaloyl dichloride (5.15 g, 25.4 mmol) dissolved in acetone (200 ml) was placed in a pressure-compensated dropping funnel and added dropwise, with stirring, to dry potassium thiocyanate (4.96 g, 51.0 mmol) dissolved in acetone (200 ml), under an inert atmosphere (N$_2$), in a three-necked, round-bottomed flask. During addition, a pale yellow precipitate formed in the reaction vessel. The mixture was heated to reflux for 45 min and then allowed to cool. Dry, distilled diethylamine (3.74 g, 51.1 mmol) was dissolved in acetone (100 ml) and added dropwise from a pressure-compensating dropping funnel into the reaction mixture under a N$_2$ atmosphere. The mixture was heated to reflux for another 45 min, after which it was allowed to cool. A pale orange solution with an off-white precipitate was observed. The mixture was transferred to a large beaker containing water (500 ml), in which the precipitate dissolved. The mixture was left to stand in a fume cupboard to allow the evaporation of acetone. After 48 h, off-white crystals of the product had formed in the beaker. The product was recrystallised from a chloroform/acetone solution by slow evaporation.

Yield: 8.50 g, 21.5 mmol, 85%, mp 141–143 °C. Found: C, 54.74; H, 6.77; N, 14.06; S, 16.01. $C_{18}H_{26}N_4O_2S_2$ requires C, 54.78; H, 6.65; N, 14.20; S, 16.25%. δ_H (200 MHz, $CDCl_3$): 1.28 (6 H, t), 1.32 (6 H, t), 3.58 (4 H, q), 4.00 (4 H, q), 7.50 (1 H, t), 7.96 (2 H, d), 8.25 (1 H, s) and 9.38 (2 H, s). δ_C (50 MHz, $CDCl_3$): 11.4 (–CH_3), 13.3 (–CH_3), 47.5 (–NCH_2–), 47.8

(–N*C*H_2–), 126.6, 129.4, 132.6, 132.8, 163.3 (–*C*(O)–) and 179.2 (–*C*(S)–).

***cis*-[Ni(I-Et-*S*,*O*)]$_2$ (1).** **H_2-I-Et** (3.946 g, 10.00 mmol) was dissolved in *N*,*N*-dimethylformamide (DMF), to which a solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ (2.489 g, 10.00 mmol) dissolved in H_2O (200 ml) and DMF (150 ml) was added dropwise while stirring vigorously at room temperature. The mixture was stirred for a further 3 h, followed by addition of H_2O (500 ml). Upon cooling to 4 °C in a refrigerator for 24 h, the dark solid product was collected by centrifugation and washed several times with small portions of water. The product, **1**, was recrystallised from chloroform/acetone to give a deep purple powder.

Yield: 3.94 g, 4.36 mmol, 87%, mp 310–313 °C. Found: C, 48.29; H, 5.47; N, 12.18; S, 13.94. $C_{36}H_{48}N_8O_4S_4Ni_2$ requires C, 47.91; H, 5.36; N, 12.42; S, 14.21%. δ_H (200 MHz, $CDCl_3$): 1.24 (24 H, m), 3.78 (16 H, m), 8.26 (6 H, m) and 8.78 (2 H, s). δ_C (50 MHz, $CDCl_3$): 12.6 (–*C*H_3), 13.1 (–*C*H_3), 45.3 (–N*C*H_2–), 45.9 (–N*C*H_2–), 126.8, 130.0, 132.5, 136.9, 170.0 (–*C*(S)–) and 172.3 (–*C*(O)–). IR (KBr, 1000–300 cm^{-1}): 943, 920, 896, 822, 779, 755, 730, 698, 679, 661, 566, 520 and 487.

Coordination polymers

Four products were synthesised by reacting metallamacrocyclic complex **1** with an *exo*-bidentate *N*-donor ligand. The same general method of preparation and collection, as described for **2** below, was applied in each case. Attempts were made to recrystallise the solid products, but these invariably met with either insolubility or a complete dissociation of the products into their separate original components, as evident from an accompanying colour change back to the original purple colour of **1**. Attempts were also made to synthesise the products more slowly by controlling the rate of mixing of the components, in order to encourage the growth of crystals suitable for single-crystal X-ray diffractometry. In each case, these attempts were unsuccessful.

Note that the yields for these products have been calculated for a coordination polymer with a MM : BL ratio of 1 : 2 and with no guests present.

{*cis*-[Ni(I-Et-*S*,*O*)(pyra-*N*,*N*′)]$_2$}$_n$ (2). Purple complex **1** (0.20 g, 0.22 mmol) was dissolved in CH_2Cl_2 (50 ml). The resultant solution was filtered through a 0.45 μm nylon filter to remove traces of solid particles. A quantity of pyra (0.16 g, 2.0 mmol) was similarly dissolved in CH_2Cl_2 and subsequently filtered. The two solutions were heated gently, mixed together in a beaker and left to stand. After a few minutes it was noted that the initially clear purple reaction mixture had developed a murky quality. After further time (*ca.* 30 min) an orange-green suspension was observed. Following a further 30 min, it was found that the suspension had thickened and separated from the mother liquor, which retained a slight tinge of purple. After another 2 h, the mother liquor was found to be clear and colourless, while the suspension was observed to be lime green. The product was centrifuged, resulting in the packing of the suspended particles into a thick disc, that, after centrifugation, rested on the upper surface of the mother liquor. The latter was decanted, after which the glass centrifuge tube, still containing the lime green solid, was placed in an oven under gentle heating to evaporate the residual solvent. The product was removed from the oven and collected as a flaking light green layer from the walls of the centrifuge tube. The product, **2**, was pulverised and then washed briefly with suction in a Buchner funnel using small amounts of ethanol/water, after which it was dried and stored as a green powder.

Yield: 0.198 g, 84.6%. Decomp. >90 °C. Found: C, 49.10; H, 5.28; N, 15.49; S, 11.77%. IR (KBr, 1000–300 cm^{-1}): 957, 945, 917, 885, 848, 831, 804, 783, 755, 726, 673, 655, 532, 486, 450, 415, 381 and 302.

{*cis*-[Ni(I-Et-*S*,*O*)(4,4′-bipyridine-*N*,*N*′)]$_2$}$_n$ (3). **1** (0.20 g, 0.22 mmol) was reacted with bipy (0.31 g, 2.0 mmol). The formation of a green suspension was noted after *ca.* 1 h. The product was collected and stored as a green powder.

Yield: 0.215 g, 80%. Decomp. >160 °C. Found: C, 54.76; H, 5.34; N, 13.77; S, 9.86%. IR (KBr, 1000–300 cm^{-1}): 956, 942, 915, 887, 847, 810, 781, 754, 723, 695, 674, 654, 627, 605, 570, 528, 493, 446 and 302.

{*cis*-[Ni(I-Et-*S*,*O*)(1,2-bis(4-pyridyl)ethane-*N*,*N*′)]$_2$}$_n$ (4). **1** (0.20 g, 0.22 mmol) was reacted with BPE (0.37 g, 2.0 mmol). The reaction mixture was left to stand. After *ca.* 1 h, a green suspension had formed. The product was collected as a green powder.

Yield: 0.212 g, 76%. Decomp. >100 °C. Found: C, 56.75; H, 5.97; N, 12.84; S, 9.13%. IR (KBr, 1000–300 cm^{-1}): 951, 918, 893, 867, 845, 827, 780, 755, 723, 693, 673, 652, 529, 468, 440 and 387.

{*cis*-[Ni(I-Et-*S*,*O*)(1,2-di(4-pyridyl)ethylene-*N*,*N*′)]$_2$}$_n$ (5). **1** (0.20 g, 0.22 mmol) was reacted with DPE (0.36 g, 2.0 mmol). The reaction mixture was left to stand. After *ca.* 1 h, a green suspension had formed. Following the same procedure as for **2** above, this product was separated from the mother liquor by centrifugation and dried with gentle heat in an oven. However, the dry flakes of solid product were found to be dull orange-pink in colour, as opposed to the green colour of the product when suspended in the mother liquor. The product was pulverised and washed with suction in a Buchner funnel using ethanol/water. Upon exposure to fumes of CH_2Cl_2, the powdered substance was observed to change colour to a bright green. On removal of the source of solvent fumes, the green powder reverted to the orange-pink colour within a few seconds. This colour change was found to be reproducible upon re-exposure to the fumes of CH_2Cl_2. This phenomenon was replicated with the use of chloroform, although a longer period of exposure to the fumes was required. It was observed that this product possesses the remarkable property of vapochromism, with an especially high sensitivity to chlorinated solvents. The process is fully reversible. The product, when dissolved in a quantity of liquid CH_2Cl_2 or chloroform, initially transformed in colour to green, but then quickly dissociated to its starting materials—indicated by the clear purple colour of the resultant solution.

Yield: 0.254 g, 91%. Decomp. >110 °C. Found: C, 56.89; H, 5.50; N, 13.29; S, 9.84%. IR (KBr, 1000–300 cm^{-1}): 966, 951, 920, 891, 849, 821, 785, 751, 724, 695, 671, 553, 487, 446 and 323. IR (KBr with DMF, 1000–300 cm^{-1}): 983, 949, 918, 889, 865, 831, 783, 752, 725, 660, 556, 446, 408, 354 and 323. The vapochromic property of the compound was recorded by digital photography. An experiment to determine the rate and extent of solvent inclusion associated with the colour change was conducted using a levitating balance.

Instrumental methods

Melting point analysis, hot stage microscopy (HSM) and digital photography. The behaviour of the ligand **H_2-I-Et** and the metallamacrocycle **1** on heating were observed using a Reichert-Jung Thermovar hot stage microscope. The proposed coordination polymers **2–5** were heated on a Linkam THMS 600 hot stage, which was controlled by a Linkam TP92 central processor. Digital photographs were taken through a Nikon SMZ-10 binocular microscope using a Sony Hyper HAD digital video camera.

Infrared spectroscopy. Samples were prepared as KBr pellets and analysed on a Perkin-Elmer 983 IR spectrometer in the 1000–300 cm^{-1} range. Product **5**, that undergoes a colour change in the presence of certain solvents, was subjected to an additional IR analysis mixed with DMF using a prepared KBr pellet. DMF was also found to effect the colour change. The lists of absorption peaks for both analyses are reported above.

Thermogravimetric analysis (TGA). Products **2–5** were subjected to TGA with a heating rate of 20 °C min^{-1} under an atmosphere of dry N_2 (flow rate: 30 cm^3 min^{-1}) using a Mettler Toleda TGA/SDTA 851^e instrument. Raw data from these analyses were plotted graphically using Microsoft Excel.

X-Ray powder diffraction (XRD). Products **2–5** were studied by XRD analysis with a HUBER-Guinier 670 Imaging Plate X-ray powder diffractometer using Cu-Kα X-rays (1.5405 Å). Graphs of X-ray reflection intensity *vs.* angle (2θ) were plotted from the raw data using Microsoft Excel.

Matrix-assisted laser desorption/ionisation time of flight mass spectroscopy (MALDI-TOF MS). Products **2–5** were submitted for MALDI-TOF MS analysis, a technique that accurately measures molecular masses of macromolecules, such as proteins. The instrument used was a Perseptive Biosystems Voyager DE-PRO Biospectrometry Workstation possessing Delayed Extraction Technology. The matrix used was a saturated solution of dithranol (DIT) in chloroform. 2 μl of the matrix/sample mixture was applied to a MALDI P100 gold sample plate and allowed to completely dry under a gentle stream of air. The drying process allowed crystallisation of the matrix and the sample was trapped in the crystals. After confirming crystal formation by light microscopy, the plate was inserted into the instrument. The sample was then analysed using the preset method HCD1005 in positive ion mode, which has an accelerating voltage of 20 kV, grid voltage of 94%, Guide Wire Voltage of 0.05% and delayed extraction at 1500 ns. Spectra were captured using Perseptive Grams/32(R) v 4.14.

Levitating balance sorption studies. Product **5**, which displays vapochromic behaviour, was subjected to levitation balance analysis.[23] A sample of the product was placed in a chamber and subsequently evacuated. CH_2Cl_2 vapour was then admitted into the chamber. A computer-controlled valve maintained constant dichloromethane pressure. Gains in sample mass due to vapour sorption were measured by a sensitive system, in which a sample pan is attached to a permanent magnet, which itself is coupled across the chamber boundary to an external electromagnet suspended from an analytical balance. This coupling is effected by maintaining the equilibrium between the upward electromagnetic and downward gravitational forces acting on the permanent magnet. Electronic feedback of the position of the permanent magnet is used to control the current through the electromagnet in order to balance the forces. Position feedback is achieved by means of optical sensing. Mass gains at various constant pressures of CH_2Cl_2 were measured over time (at room temperature). The raw data were plotted graphically using Microsoft Excel.

The following are available as ESI: TGA plots and HSM photographs of **2–5**; digital photographs and gravimetric studies of **5**.†

Results and discussion

Synthesis and elemental analysis

Treatment of the readily-soluble, purple diamagnetic complex *cis*-[Ni(I-Et-*S*,*O*)]$_2$ (**1**) with the series of bridging *N*-donor ligands studied in this paper resulted in sparingly-soluble to insoluble green powder-like compounds of relatively consistent composition. Numerous attempts to grow crystals of these green compounds, indicative of Ni(II) in an octahedral coordination environment, unfortunately failed.

Infrared spectroscopy. Infrared analysis was performed on metallamacrocycle **1**, each of the four bridging ligands and the products **2–5**. There are certain features in the various IR spectra that indicate significant differences between **1** and its proposed polymerisation products **2–5**. Primarily, an absorption peak characteristic of the free metallamacrocycle at 487 cm^{-1} is conspicuously absent in the spectra of products **3** and **4**, as well as that of **5** in the presence of DMF. The absence of this peak at 487 cm^{-1} from the spectra of **3** and **4** indicates that in those products, the metallamacrocycles are somehow bound; a further indication that these products are indeed polymeric. A peak is present nearby in the spectrum of **2** (at 486 cm^{-1}), but in that case is attributed to pyra. In fact, it confirms that pyra is acting as an *exo*-bidentate ligand, since the shifting of a peak at *ca.* 417 cm^{-1} in the spectrum of free pyra to 472–486 cm^{-1} in the spectrum of a pyra complex is characteristic of the pyra acting as a bidentate bridging ligand.[15a,b] The peak that remains in the spectrum of **2** at 415 cm^{-1} suggests that pyra is present in this product as a guest as well as in a coordinated state.

Some vital information can be gleaned from the initial presence of the peak at 487 cm^{-1} in the spectrum of **5**, and its subsequent disappearance when DMF is used to induce the colour change. This observation points to the presence of free metallamacrocycle in the structure of **5**. The absence of a peak in the spectrum of **5** with DMF at *ca.* 670 cm^{-1} also strengthens this argument. This peak is observed for pure DPE and also for the solvent-free **5**, and apparently arises from a vibrational mode available to free DPE but not to coordinated DPE. These results therefore indicate that DPE and the metallamacrocycle are present in the structure of **5**, both in an uncoordinated state. Exposure of **5** to DMF (and presumably any other solvent that is able to induce the change in state of the product) seems to cause the free metallamacrocycle and DPE to undergo axial coordination, which results in the disappearance of the peaks at 487 cm^{-1} and 670 cm^{-1}.

Thermal analysis. Table 1 summarises the results of the thermal analysis of the four coordination polymers of **1**. In each case, a rapid mass loss occurs at or close to 310 °C. This is taken to indicate the decomposition of **1**, suggesting that the remaining mass just prior to this final decomposition can be attributed to the metallamacrocycle. All calculations of preceding mass losses are based on this premise.

For **2**, the M : B : S ratio is calculated as 1 : 8 : 0. If the compound is a coordination polymer with two coordinated pyras per metallamacrocycle, then the remaining pyras should be present as guests. The order of mass loss in the TGA bears this out, with the six guest pyras lost fairly early, followed by the loss of the two coordinated pyras. This confirms the results of IR analysis, which indicated the presence of uncoordinated pyra molecules in the compound.

In the case of **3**, the results of TGA can clearly be interpreted as signifying the loss of one bipy, followed by one CH_2Cl_2 molecule, and finally the loss of three molecules of bipy. Thus **3** has a M : B : S ratio of 1 : 4 : 1, and if it is a coordination polymer, two bipys act as bridging ligands, while the other two are present as guests. It may seem counter-intuitive that one

Table 1 Results of TGA for products **2–5**

Compound	**2**: Molecular formula $[C_{36}H_{48}N_8O_4S_4Ni_2]\cdot(C_4H_4N_2)_8$				**3**: Molecular formula $[C_{36}H_{48}N_8O_4S_4Ni_2]\cdot(C_{10}H_8N_2)_4\cdot CH_2Cl_2$			
Feature	T/°C	Mass (%)	Molar mass/g mol^{-1}	Component	T/°C	Mass (%)	Molar mass/g mol^{-1}	Component
Onset of final decomposition	306	58.51%	902.51	**1**	308	56.14%	902.51	**1**
1st mass loss	29–114	31.37%	484	6 pyra	163–220	9.98%	160	1 bipy
2nd mass loss	114–162	4.87%	75	1 pyra	220–239	5.29%	85	1 CH_2Cl_2
3rd mass loss	162–197	5.26%	81	1 pyra	239–308	29.20%	469	3 bipy
Total mass loss	29–197	41.50%	640	8 pyra	163–308	44.50%	718	4 bipy + 1 CH_2Cl_2

Compound	**4**: Molecular formula $[C_{36}H_{48}N_8O_4S_4Ni_2]\ (C_{12}H_{12}N_2)_3\cdot CH_2Cl_2$				**5**: Molecular formula $[C_{36}H_{48}N_8O_4S_4Ni_2]\cdot(C_{12}H_{10}N_2)_{0.5}$			
Feature	T/°C	Mass (%)	Molar mass/g mol^{-1}	Component	T/°C	Mass (%)	Molar mass/g mol^{-1}	Component
Onset of final decomposition	304	60.20%	902.51	**1**	310	70.77%	902.51	**1**
1st mass loss	179–205	2.81%	42	Unassigned	196–263	19.33%	246	1.3 DPE
2nd mass loss	205–237	8.26%	124	Unassigned	263–310	10.40%	133	0.7 DPE
3rd mass loss	237–304	29.27%	439	Unassigned				
Total mass loss	179–304	40.34%	605	3 BPE + 1 CH_2Cl_2	163–308	29.73%	378	2 DPE

bipy guest should be removed very early in the heating cycle, while the other remains until the coordinated bipys are removed. This can be explained if the second bipy guest is trapped in the structure in such a way that it cannot leave until the bridging ligands leave, effectively leading to the destruction of the polymeric structure. A similar phenomenon was observed for the related compounds of the 2 : 2 metallamacrocycle with axially-coordinated pyridine and 4-dimethylaminopyridine ligands.[2]

For compound **4**, the TGA results for individual mass loss events did not fit any integral (or simple fraction) numbers of BPE or CH_2Cl_2 molecules, and thus no assignment could be made. However, the mass calculation for a model with a M : B : S ratio 1 : 3 : 1, indicates that 41.4% of the total mass would be attributed to BPE and CH_2Cl_2, which is consistent with the total mass loss of 40.34% observed up to 304 °C.

The TGA results for **5** are interesting. Overall, the calculations show that the compound loses 2 DPEs per metallamacrocycle. In other words, **5** exists in a guest-free state without being subjected to a vacuum. This is a deviation from the behaviour of the other compounds and explains why **5** alone displays vapochromism, as will be discussed below. It is noteworthy that the two individual mass loss events do not correspond to integral numbers of DPE, but rather losses first of *ca.* 1.3 DPEs followed later by *ca.* 0.7 DPE, resulting in approximately the mass ratio 2 : 1. Since IR indicates that both free and coordinated DPE are present in **5**, it is logical to conclude that the first event corresponds with the removal of the free DPE and the second with the removal of the coordinated DPE.

Hot stage microscopy. The behaviour of each of the compounds was observed while being heated under silicone oil. Products **2–4** all display similar behaviour. Starting as a green powder, they transform through an orange-coloured intermediate phase into a purple product with concomitant evolution of gas, evident from the appearance of bubbles in the oil. The temperature range of colour transformation varies from one product to the next. **2** transforms in the range 90–240 °C, **3** from about 100–225 °C and **4** from 100–230 °C. This colour change is clearly associated with the breaking of the axial coordination of the *N*-donor ligands to the Ni(II) centres of the metallamacrocycles. As has been shown for the monomeric octahedral pyridine complexes of **1** and a similar metallamacrocycle,[2,10] the purple colour arises from a square planar Ni(II) complex, while the green colour arises from an octahedral Ni(II) environment. The orange intermediate colour thus indicates the presence of both coordination states within the sample, part way through the transformation. The bubbling is attributed to the removal of guests and bridging ligands from the structure.

Compound **5** behaves differently during HSM. It begins as an orange-brown powder and gradually transforms, with bubbling, into a purple powder in the temperature range 100–240 °C. As suggested for compounds **2–4**, the orange colour is indicative of a mixture of square planar and octahedral Ni(II) environments in the sample. We speculate that this compound is initially in a state in which only some of the Ni(II) centres have DPE molecules coordinated to them. On heating, the existing N–Ni bonds are broken and the sample reverts fully to the square planar metallamacrocycle as the DPE is expelled. This quasi-porous structure is consistent with the other unusual solvatochromic behaviour observed for this compound (*vide infra*).

As deduced from the TGA, **5** has a M : B : S ratio of 1 : 2 : 0, *i.e.* the correct amount of DPE for a coordination polymer. However, the orange colour suggests that it is not a true coordination polymer, since not all of the DPEs are coordinated to Ni(II) centres, consistent with the IR spectroscopic results discussed earlier.

X-ray powder diffraction. For each of the compounds **2–5**, an X-ray powder pattern was obtained and compared to that of **1**, as well as to the pattern of the relevant bidentate *N*-donor compound and a superposition of the pattern of **1** onto that of the bidentate compound (Fig. 4.) In each case, it is clear that the product is microcrystalline and possesses a different crystal structure. These compounds are thus not physical mixtures of **1** and the bridging bidentate ligand. This is seen quite easily by the appearance of new peaks in the diffraction pattern of the product, or indeed the disappearance of peaks that were present in the traces of the ligand or **1**. In each case, peak broadening is observed in the pattern of the product as compared with the patterns of its parent compounds. This could be indicative of a lower degree of crystallinity for the new products.

While all compounds **2–5** have similar XRD traces (indicating the similarity of the crystalline phases formed) those of **2**

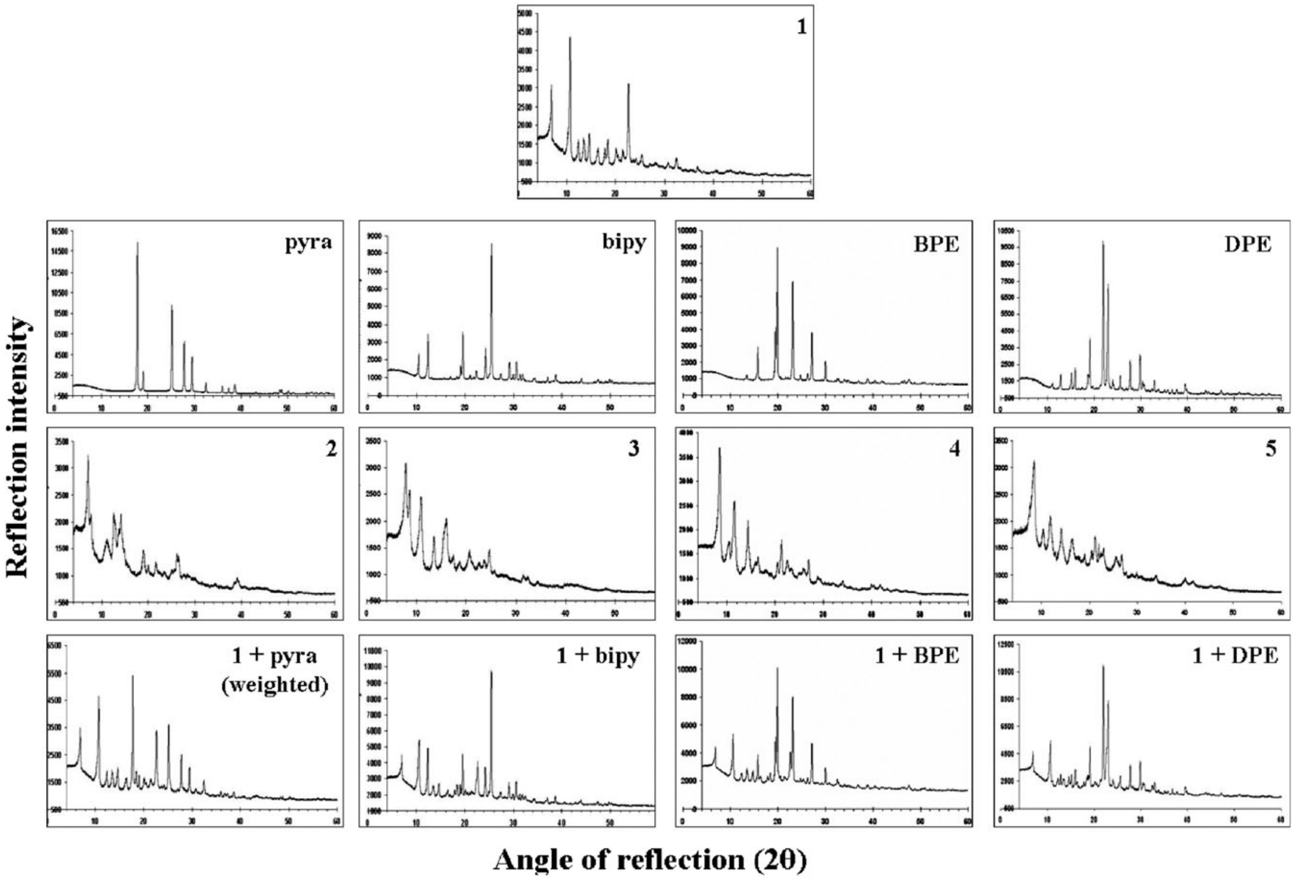

Fig. 4 X-ray powder diffraction patterns for compounds **2–5** (3rd row) compared with those of **1** (top row) and the various *exo*-bidentate ligands (2nd row), from which they are formed. Superpositions of the pattern of **1** onto the patterns of the ligands are provided in the bottom row.

and **3** are significantly different to each other and to those of **4** and **5**. This is to be expected given that pyra and bipy have very different sizes and topologies to BPE and DPE. It should however be noted that compounds **4** and **5** have virtually identical powder patterns, as shown in Fig. 5. The only variations between the patterns are marginally shifted angles and, in general, higher peak heights for **4**. This similarity is a strong indication that the two products possess similar crystal structures. Given the similarity in structure of the two bridging ligands BPE and DPE, this result is not unexpected. Nevertheless, the one slight difference between the two ligands (the two central carbons being saturated in BPE *vs.* unsaturated in DPE) appears to be enough to result in the marked difference in behaviour between **4** and **5**.

Product **5** was also exposed to vapours of CH_2Cl_2 and analysed by XRD in the continued presence of the vapour. The result was a broad, featureless trace. This suggests that CH_2Cl_2 disrupts the crystal structure of **5** as it interacts with it. It is possible that CH_2Cl_2 is not only taken up as a guest in the structure, but also partially dissolves the structure. On removal of the CH_2Cl_2 vapour, the material rapidly changed colour and peaks were again observable in the XRD trace. Peak widths were constant through several absorption/desorption cycles.

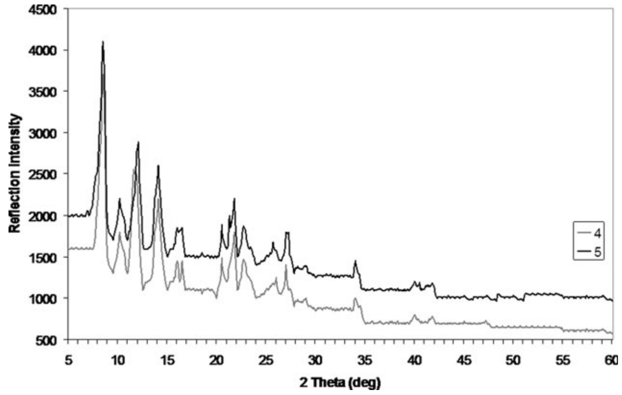

Fig. 5 Comparison of X-ray powder diffraction patterns of **4** (grey) and **5** (black). The two traces are virtually identical, indicating similar crystal structures.

MALDI-TOF mass spectroscopy. Since elemental and thermal analysis indicate the predicted stoichiometry for coordination polymers, products **2–5** were analysed by MALDI-TOF MS to determine the number of repeating units in the coordination polymers. In each case, however, the only mass peaks observed were those corresponding to single metallamacrocyclic units, *i.e. ca.* 0.90 kDa (kg mol^{-1}).

It is believed that the solvent used in the technique caused the polymers to dissociate into their separate components, as the results presented above offer both compelling qualitative and quantitative evidence of this, suggesting that the products are indeed polymeric, with the notable exception of **5**. As a result of this phenomenon, MALDI-TOF MS proved not to be useful in analysing these products.

Levitating balance sorption measurements. The results of the analysis of **5** indicate that it has the correct stoichiometry for a guest-free coordination polymer, but that it is not initially in a fully coordinated state. The exposure of **5** to solvent molecules such as CH_2Cl_2 induces a transformation into the fully coordinated state, which is observed qualitatively as a change in colour from orange to green. The uptake of solvent molecules by **5** was observed gravimetrically by use of a sensitive levitating balance in a closed system. The sample was weighed (155 mg) and then placed in an evacuated chamber. CH_2Cl_2 was then allowed to enter the chamber to a fixed pressure, and

Table 2 Results of levitating balance study of CH_2Cl_2 sorption by **5**

Molar mass of **1**/g mol^{-1}	902.508		
Molar mass of DPE/g mol^{-1}	182.226		
Molar mass of 1 repeating unit of **5**/g mol^{-1}	1266.96		
Mass of sample/g	0.155		
No. of moles of repeating units	1.22×10^{-4}		
Molar mass of CH_2Cl_2/g mol^{-1}	84.933		
Pressure of CH_2Cl_2/mmHg	200	250	300
Mass of sorbed CH_2Cl_2/g	0.053	0.067	0.069
No. of moles of CH_2Cl_2 sorbed	6.24×10^{-4}	7.89×10^{-4}	8.12×10^{-4}
No. of CH_2Cl_2 molecules sorbed per repeating unit	5.10	6.45	6.64

isobaric measurements of sample mass gain over time were taken. The experiment was repeated at different pressures from 200–300 mmHg. It was found that the pressure of the solvent in the chamber affects the amount of solvent sorbed by the sample, so that at 200 mmHg, the sample sorbs a maximum of 53 mg of CH_2Cl_2, at 250 mmHg, the sample sorbs a maximum of 67 mg and at 300 mmHg, the sample sorbs a maximum of 69 mg. The mass gains levelled off within 30 min in each case, indicating that the process is one of absorption rather than solvascopic adsorption.

These results reveal that **5** is a strong solvent sorbing agent, able to take-up almost half its own mass of CH_2Cl_2 at the highest pressure. This effect certainly involves the penetration of the internal structure of **5** and is not merely the result of adsorption onto the surface of the sample. This is a strong indication that **5** has a porous structure, through which solvent molecules can travel with relative ease.

Table 2 shows a calculation of the number of CH_2Cl_2 molecules sorbed per repeating unit in the structure of **5**. At the highest pressure, more than 6.5 molecules of CH_2Cl_2 per metallamacrocyclic unit are absorbed. The values are clearly non-stoichiometric, suggesting that while there are possibly specific sites within the structure which must be occupied by solvent molecules to induce the coordination of DPE to Ni(II) and the associated colour change, it seems that these sites are not the only positions within the structure available for solvent molecules. The higher the pressure of the solvent vapour, the more solvent molecules penetrate and disrupt the structure, hence the featureless XRD trace for **5** when exposed to CH_2Cl_2. However, upon removal of the vapour, the sorbed solvent molecules exited the structure just as easily as they entered it, leaving it intact.

Vapochromism. Exposure of **5** to various solvents reveals the vapochromic property of the product, which may be associated with a conversion from free metallamacrocycle and DPE to their coordinated forms. This is illustrated for CH_2Cl_2 in Fig. 6. While the XRD patterns suggest that **4** and **5** have similar crystal structures, that of **5** may be more porous, as it clearly takes up CH_2Cl_2, in contrast to **4**. Vapochromic mechanisms vary, but often appear to require small disruptions to the crystal structure upon absorption of solvent molecules. It is clear that this issue needs further investigation since very little is known about the exact mechanism of this effect in **5**. The fully elucidated crystal structure of this product would be very useful for the purpose of determining this mechanism, and efforts to obtain such information are under way.

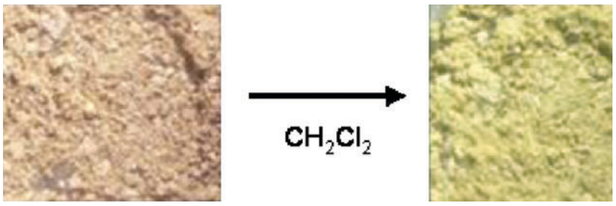

Fig. 6 Vapochromic behaviour of **5**: (i) orange powder prior to vapour exposure, (ii) pale green powder after *ca.* 1 min exposure to CH_2Cl_2 vapour.

Conclusion

Compounds **2–4** are coordination polymers of a new and interesting type, having been designed and assembled from the 2 : 2 metallamacrocycle **1**, linked by bidentate *N*-donor ligands, with additional molecules included in their structures as guests. These compounds clearly warrant additional study. In particular, full crystal structures and data on their polymer sizes are greatly desired. Furthermore, studies based on molecular models predict that other types of polymeric arrays can be assembled in a similar manner, provided that bridging ligands long enough to circumvent any steric restrictions are used. Similar polymers may also be formed from the analogous 3 : 3 metallamacrocycles.[3]

Product **5** is unique. Results show that **5** has the correct stoichiometry for a coordination polymer with a marked tendency to selectively absorb significant amounts of CH_2Cl_2, and may thus be considered as a potential sensor for chlorinated hydrocarbon molecules. Future studies of this compound's behaviour are imperative and may yet yield possible applications for its remarkable properties.

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