Molecular Tectonics: Design of 1-D Coordination Networks Based on Pyrene-Bearing Pyrazolyl Units

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The synthesis of a new ligand based on a pyrene backbone bearing four pyrazolyl units is reported. Whereas this compound forms a discrete exo-binuclear complex with palladium, in the presence of silver a 1-D coordination network is obtained and structurally characterised in the solid state by X-ray diffraction method.

Introduction

Coordination networks i.e. periodic molecular assemblies formed by the self-assembly of organic and metallic tectons (active molecular building blocks) has attracted increasing interest over the last decade.[1] The formation of coordination networks results from the interconnection of metallic centres by organic ligands through coordination bonds. Both the metal centre and the organic ligand must permit the iteration of the coordination process in order to behave as tectons.[2] In other words, the organic tecton must posses at least two coordination sites or poles[3] divergently oriented. The dimensionality of the network depends on the number of translations of the coordination pattern in different directions of space. Thus, a 1-D coordination network is generated by a single translation of the coordination pattern. For the design of coordination networks, one must take into account the interplay between the organic (number of coordination sites, topology) and metallic (number of coordination and geometry) tectons. For 1-D coordination networks, the majority of cases reported deal with bis-monodentate tectons.[4] However, a few examples of bis-bidentate[5,6] bis-tridentate[7−9] and a combination of mono- and tridentate[3] tectons have been also published.

Here we report the formation of the 1-D coordination network **7** formed between the pyrene-based tecton **4**, bearing four pyrazolyl units, and the silver cation, and the synthesis of two discrete binuclear palladium complexes **5** and **6**.

Results and Discussion

As stated above, examples of coordination networks containing bis-chelate tectons are rather rare. In a continuation of our efforts towards the design of new types of coordination networks,[10] we thought that the pyrene-based tecton **4** bearing four pyrazolyl units may be of interest for the formation of 1-D coordination networks in the presence of connecting transition metals. The synthesis and binding ability of pyrazole-based ligands have been reported.[11] The design of the tecton **4** was based on the use of pyrene as the backbone because the latter permits the introduction of four monodentate units in positions 4, 5, 9 and 10 in a symmetrical fashion. The pyrazolyl group was the obvious candidate as the monodentate unit. Indeed, when four such units are connected through their nitrogen atoms to the pyrene backbone at positions 4, 5, 9 and 10, due to their localisation, each set of two pyrazolyl units on each side of the backbone will behave as a chelate, thus affording a bis-chelate tecton. Pyrene has previously been used as a backbone to anchor bipyridine,[12,13] terpyridine[13] and quinoline[14] units. Due to its planarity, pyrene **1** is poorly soluble in common solvents, and so we thought that the introduction of bulky and nonplanar *tert*-butyl substituents at positions 2 and 7, remote from the binding zones of the ligand, should overcome this insolubility problem.

For the synthesis of compound **4**, pyrene **1** was the starting material. The introduction of the *tert*-butyl groups at positions 2 and 7, leading to compound **2**, was achieved following reported procedures.[15] The bromination of **2** by Br_2 in the presence of $FeCl_3$ in CCl_4, leading to the tetrabromo compound **3**, was also achieved following reported procedures.[16] Finally, the desired compound **4** (Scheme 1) was obtained in 24% yield upon treatment of the tetrabromo compound **3** with sodium pyrazolate in DMF.

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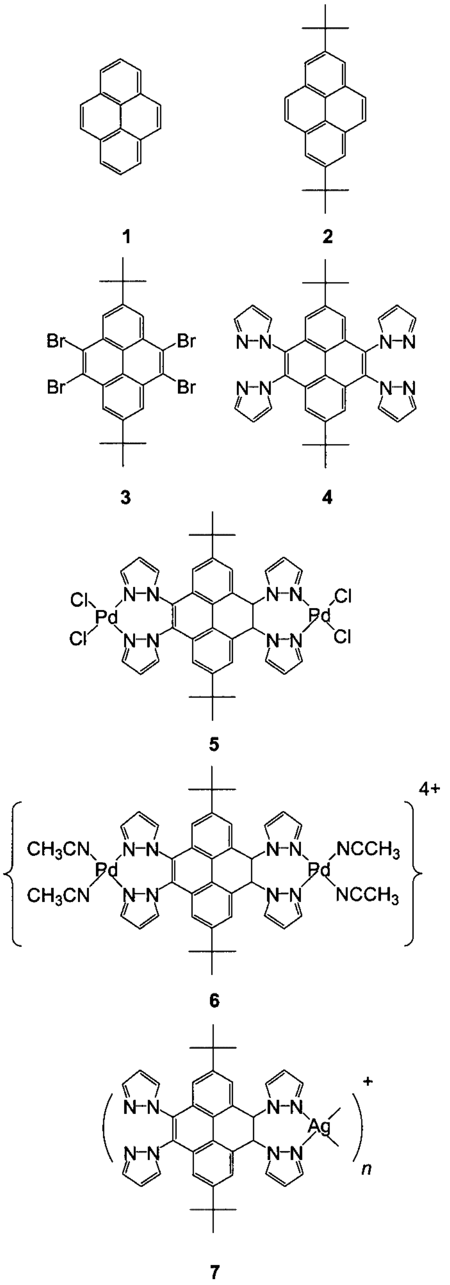

Scheme 1

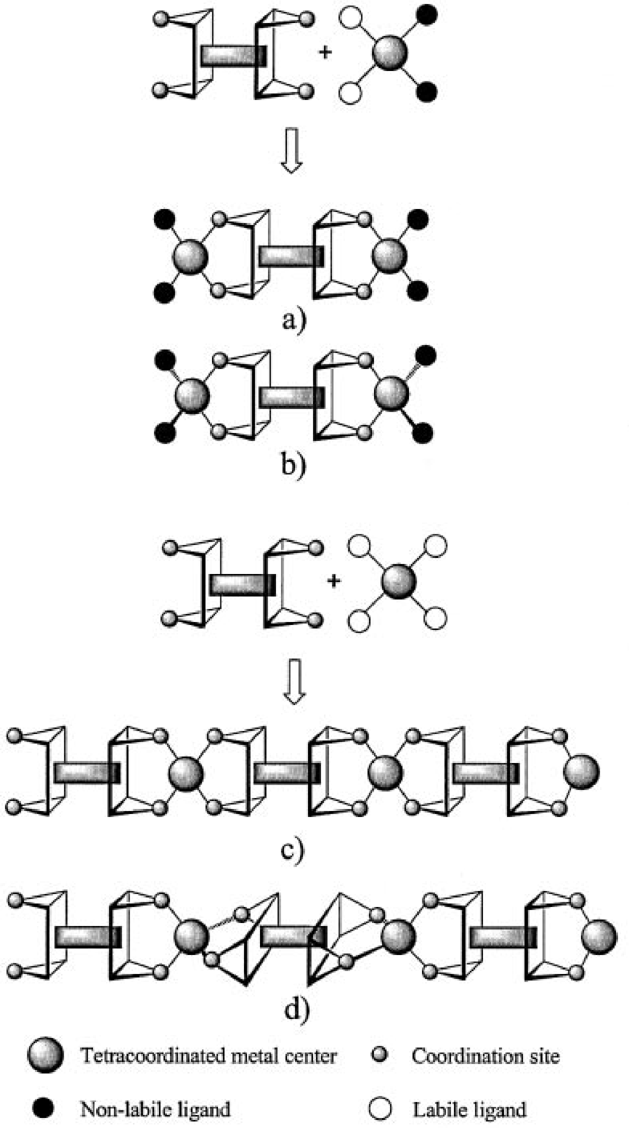

Figure 1. Schematic representation of the formation of discrete exo-binuclear complexes formed between an exo-bis-chelate ligand and deprotected metal centres adopting a square planar (a) or tetrahedral (b) coordination geometry, or infinite 1-D coordination networks in the presence of metal centres adopting a square planar (c) or tetrahedral (d) coordination geometry

Among many coordination possibilities that the bis-chelate tecton **4** may offer, one may envisage the formation of discrete exo-binuclear complexes upon binding of metal centres possessing only two available coordination sites and adopting either a square planar (Figure 1a) or a tetrahedral (Figure 1b) coordination geometry.

The quantitative formation of the exo-binuclear palladium complex **5** was demonstrated by treating the ligand **4** with [PdCl$_2$(CH$_3$CN)$_2$] in a mixture of CH$_2$Cl$_2$ and CH$_3$CN at room temperature. Complex **5** is rather insoluble in common solvents. However, suitable yellow-orange single-crystals could be obtained from a DMSO/MeOH mixture. The structure of **5** was investigated in the solid state by X-ray diffraction, which revealed the following features (Figure 2). The crystal (triclinic, space group $P\bar{1}$) is composed of discrete binuclear complexes **5**, two DMSO and one water solvent molecules. Although the H$_2$O molecule is H-bonded to the O atom of DMSO (d_{O-O} = 2.74 Å), no specific interactions between the solvent molecules and complex **5** could be identified. For the pyrene moiety, possessing a centre of symmetry, the aromatic core, as expected, is planar. Both *tert*-butyl groups are disordered over two positions. The pyrazolyl units [average N−N distance of ca 1.35 Å and $d_{N-C(Py)}$ = 1.43 Å] are tilted with respect to the plane of pyrene (NNCC dihedral angles of −69° and 73.9°). The two sets of two pyrazolyl units forming two chelates are located above and below the main plane of the ligand. Consequently, the two square-planar Pd centres are also located above and below the main plane of the pyrene backbone. The coordination sphere around each Pd^{II} is composed of two N atoms belonging to two adjacent pyrazolyl units in *cis* configuration (average d_{Pd-N} of 2.03 Å, NPdN angle of ca 88°) and two Cl^- anions (d_{Pd-Cl} = 2.28 Å, ClPdCl angle of ca 92°).

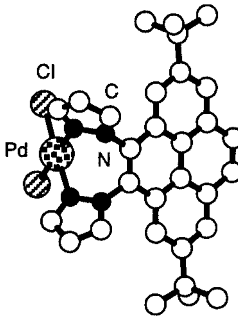

Figure 2. Crystal structures of the exo-binuclear palladium complex formed with pyrazolyl-based ligand **4**; solvent molecules (DMSO, H_2O) and H atoms are omitted for clarity; for bond lengths and angles see text

When dealing with 1-D coordination networks based on bidentate tectons, many structural frameworks may be envisaged.[17] In particular, in the presence of the tecton **4**, 1-D networks may be generated by using tetracoordinate metal centres adopting either a square planar (Figure 1c) or tetrahedral (Figure 1d) coordination geometry.

Since the Cl^- anions bound to Pd^{II} are not sufficiently labile for generating a network in the presence of free tecton **4** (neutral ligand), the binuclear complex **6**, for which the Cl^- anions are substituted by acetonitrile molecules and the positive charge on the complex is compensated by tetrafluoroborate anions, was prepared in quantitative yield upon treatment of **4** with $[Pd(CH_3CN)_4][BF_4]_2$ in a mixture of CH_2Cl_2 and CH_3CN at room temperature. The much more soluble complex **6** was characterised by NMR spectroscopy. Considering the discrete complex **6** as a metalla tecton, the formation of a 1-D network of the square-planar type shown in Figure 1c was attempted in the presence of the free ligand **4**. Unfortunately, crystallisation under different conditions (variation of the solvent and co-solvent, temperature) afforded only an amorphous and insoluble powder which could not be structurally characterised.

The formation of 1-D networks **7** of the tetrahedral type presented schematically in Figure 1d was investigated using the Ag^+ cation, which may adopt a tetrahedral coordination geometry. In a crystallisation tube, upon slow diffusion of a solution of $Ag(PF)_6$ (10 mg, excess) in EtOH (3 mL) into a solution of compound **4** (5 mg) in $CHCl_3$ (2 mL), colourless crystals of network **7** were obtained at room temp. in the dark over a period of a week and studied by X-ray diffraction of a single crystal (Figure 3). The crystal (triclinic system, space group $P\bar{1}$) is composed of **4**, the Ag^+ cation, a PF_6^- anion and $CHCl_3$ solvent molecules. Although the $CHCl_3$ molecule is rather weakly H-bonded to the PF_6^- anion (d_{H-F} = 2.35 Å), no specific interactions between the cationic part of the crystal and the solvent or anion could be observed.

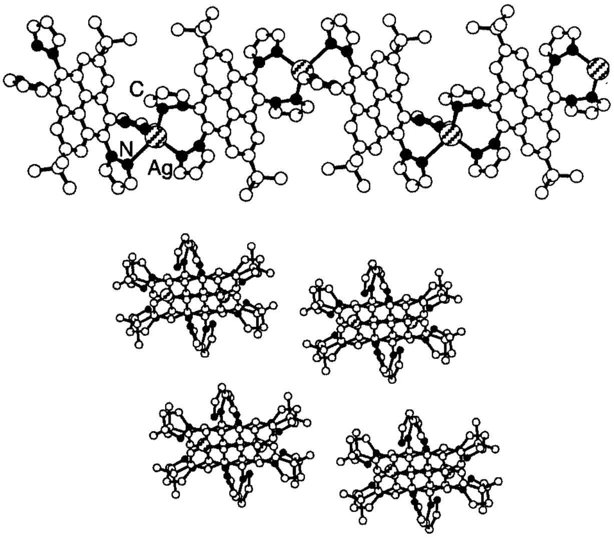

Figure 3. A portion of the crystal structures of the stair-type, 1-D coordination network formed by the self-assembly of **4** and Ag^+ cation (top) and the parallel packing of the 1-D networks (bottom); anions (PF_6^-), solvent molecules ($CHCl_3$) and H atoms are omitted for clarity; for bond lengths and angles see text.

The cationic portion of the crystal is an infinite coordination network formed upon interconnection of the organic tectons **4** by silver cations (Figure 3 top). As in the case of the square-planar discrete binuclear Pd complex mentioned above, the pyrazolyl units are tilted with respect to the plane of pyrene (NNCC dihedral angles of −82.3° and 85.0°) and located on the opposite faces of the centrosymmetric ligand **4**, thus offering two chelates, one on each face of the ligand. The coordination sphere around the silver cation is composed of four N atoms (d_{Ag-N} varying between 2.24 Å and 2.50 Å) belonging to two sets of two pyrazolyl units of consecutive ligands. The coordination geometry around the silver cation is a severely distorted tetrahedron (NAgN angle varying between 84.7° and 139.7°). The stair-type 1D network **7** may be described as the translation into a single direction of space of the coordination node composed of a tetracoordinate silver cation and two sets of two pyrazolyl units belonging to two consecutive ligands **4**. The cationic 1-D networks are packed parallel to each other (Figure 3 bottom) and the empty spaces are occupied by chloroform molecules.

In summary, the synthesis of the new ligand **4** based on a pyrene backbone bearing four pyrazolyl units was achieved. Whereas the compound **4** was shown to bind two PdX_2 moieties (X = Cl^- or CH_3CN) to form the exo-binuclear palladium complexes **5** and **6**, respectively, in the presence of $AgPF_6$, the formation of a 1-D coordination network **7** based on the interconnection of the organic tecton **4** by silver cation adopting a tetrahedral coordination geometry was demonstrated in the solid state by X-ray diffraction on single-crystal. The preparation of either other discrete complexes or coordination networks using the ligand **4** and other transition metals is currently under investigation.

Experimental Section

Synthesis of 4: NaH (50% in oil, 0.69 g, 14.3 mmol) was added in small portions to a solution of pyrazole (1 g, 14.7 mmol) in dry DMF (45 mL) under argon and the mixture stirred at room temperature for 35 min. A solution of the tetrabromo compound **3** (1.0 g, 1.58 mmol), prepared according to published procedures,[16] was added to this mixture in one portion. The mixture turned blue instantaneously. Upon heating the mixture at 130 °C for 40 h., a dark red solution was obtained. The solvents were evaporated to dryness and the residue was taken up in water (50 mL). The brownish solid was filtered, washed with water (50 mL) and finally dried under vacuum. The pure compound **4** (0.22 g) was obtained in 24% yield after column chromatography (SiO_2, CH_2Cl_2, 0−1% MeOH). m.p. > 300 °C, ^1H NMR ($CDCl_3$, 200 MHz, 25 °C): $\delta = 1.33$ (s, 18 H, CH_3), 6.37 (t, 2 Hz, 4 H, $H_{pyrazolyl}$), 7.48 (d, 2 Hz, 4 H, $H_{pyrazolyl}$), 7.86 (d, 2 Hz, 4 H, $H_{pyrazolyl}$), 7.98 (s, 4 H, H_{pyrene}) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 31.4$, 106.7, 122.0, 127.7, 133.0, 133.1, 141.3, 151.1 ppm. $C_{36}H_{34}N_8$: (578.72): calcd. C 74.72, H 5.92, N 19.36; found C 74.33, H 5.88, N 19.12.

Synthesis of 5: A solution of $[PdCl_2(CH_3CN)_2]$ (18 mg, 0.069 mmol) in CH_3CN (4 mL) was added to a solution of **4** (20 mg, 0.035 mmol) in CH_2Cl_2 (3 mL) under argon and the mixture stirred overnight at room temperature. The solvents were evaporated to dryness and the residue was taken up in CH_2Cl_2 (5 mL) and filtered. The solid was further washed with diethyl ether (10 mL). The pure complex **5** obtained in quantitative yield (32 mg) was insoluble in all common solvents. ^1H NMR (DMSO, 200 MHz, 25 °C): $\delta = 1.29$ (s, 18 H, CH_3), 6.51 (broad, 4 H, $H_{pyrazolyl}$), 6.99 (broad, 4 H, $H_{pyrazolyl}$), 8.27 (s, 4 H, H_{pyrene}), 8.86 (broad, 4 H, $H_{pyrazolyl}$) ppm. $C_{36}H_{34}Cl_4N_8Pd_2 \cdot CH_3CN$ (974.4): calcd. C 46.84, H 3.83, N 12.94; found C 46.70, H 3.60, N 12.72.

Synthesis of 6: A solution of $[Pd(CH_3CN)_4][BF_4]_2$ (50 mg, 0.11 mmol) in a 1:1 mixture of CH_3CN and CH_2Cl_2 (10 mL) was added to a solution of **4** (30 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) under argon and the mixture stirred overnight at room temperature. The solvents were evaporated to dryness affording the desired complex in quantitative yield. ^1H NMR (CD_3CN, 200 MHz, 25 °C): $\delta = 1.45$ (s, 18 H, CH_3), 2.17 (s, 12 H, CH_3CN), 7.06 (t, J = 1.6 Hz, 4 H, $H_{pyrazolyl}$), 8.03 (s, 4 H, H_{pyrene}), 8.42 (d, J = 1.5 Hz, 4 H, $H_{pyrazolyl}$), 8.55 (d, J = 1.5 Hz, 4 H, $H_{pyrazolyl}$) ppm.

Crystallisation Conditions

Complex 5: In a crystallising tube, MeOH was slowly diffused into a solution of **5** in DMSO at room temperature affording, after several days, yellowish-orange crystals.

Network 7: In a crystallising tube, a solution of $AgPF_6$ (excess, 10 mg) in EtOH was slowly diffused into a solution of **5** (5 mg) in $CHCl_3$ at room temperature and in the dark. After a week, colourless crystals were obtained.

Crystal Structure Characterisation: X-ray diffraction data collection was carried out on a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K_α radiation. For all structures, diffraction data were corrected for absorption and analysed using OpenMolen package.[18] All non-H atoms were refined anisotropically.

Crystallographic Data for 5 (Yellow Crystals, 294 K): $C_{36}H_{34}Cl_4N_8Pd_2 \cdot 2DMSO \cdot H_2O$, $M = 1107.62$, triclinic, $a = 13.1079(3)$, $b = 13.6607(4)$, $c = 15.1388(4)$ Å, $\alpha = 92.145(5)$, $\beta = 99.638(5)$, $\gamma = 115.715(5)$, $U = 2389.3(4)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_{calcd.} = 1.54$ g cm^{-3}; $\mu = 1.108$ mm^{-1}, 5800 data with $I > 3\sigma(I)$, $R = 0.054$, $Rw = 0.087$.

For 7 (Colourless Crystals, 173 K): $C_{36}H_{34}AgN_8 \cdot PF_6 \cdot 4CHCl_3$, $M = 1309.07$, triclinic, $a = 11.4299(4)$, $b = 15.5450(5)$, $c = 17.8274(6)$ Å, $\alpha = 103.614(5)$, $\beta = 101.712(5)$, $\gamma = 110.022(5)$, $U = 2749.5(6)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_{calcd.} = 1.58$ g cm^{-3}; $\mu = 1.037$ mm^{-1}, 6900 data with $I > 3\sigma(I)$, $R = 0.085$, $Rw = 0.096$.
CCDC-193060 (**5**) and 193061 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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