

plexes and extended networks can be envisaged to elaborate new supramolecular magnetic materials (high-spin molecules and molecular-based magnets).

Experimental Section

H₄[1]: The proligand was prepared in a standard manner^[18] from the condensation of 1,3-phenylenediamine and ethyl oxalyl chloride in THF, and was isolated as the diethyl ester derivative (90%). Elemental analysis calcd (%) for C₁₄H₁₆N₂O₆ (308): C 54.55, H 5.19, N 9.09; found: C 54.57, H 5.18, N 9.04; ¹H NMR ([D₆]DMSO): δ = 1.32 (t, 6H; 2CH₃), 4.31 (q, 4H; 2CH₂O), 7.34 (dt, 1H; 5-H of C₆H₄N₂), 7.50 (dd, 2H; 4-H and 6-H of C₆H₄N₂), 8.22 (t, 1H; 2-H of C₆H₄N₂), 10.83 (s, 2H; 2NH); ¹³C NMR ([D₆]DMSO): δ = 14.17 (2CH₃), 62.71 (2CH₂O), 113.25 (2-C of C₆H₄N₂), 117.45 (4-C and 6-C of C₆H₄N₂), 129.34 (5-C of C₆H₄N₂), 138.08 (1-C and 3-C of C₆H₄N₂), 156.13 (2-C(O)NH), 161.02 (2CO₂); IR (KBr): $\tilde{\nu}$ = 3349 (N–H), 2979, 2943 (C–H), 1725, 1715, 1698 cm^{−1} (C=O); UV/Vis (THF): λ_{max} (ϵ) = 335 nm (800).

Complex **2** was obtained following a reported procedure^[18] by reaction of the diethyl ester derivative of the ligand with Cu²⁺ ions in basic aqueous media, and isolated as its octahydrate sodium salt (85%). Elemental analysis calcd (%) for C₂₀H₂₄Cu₂N₄Na₄O₂₀ (859): C 27.94, H 2.79, N 6.52; found: C 27.77, H 2.62, N 6.40; IR (KBr): $\tilde{\nu}$ = 3423 (O–H), 1659, 1597 cm^{−1} (C=O); UV/Vis (H₂O): λ_{max} (ϵ) = 645 (150), 380sh (1600), 345 nm (2650). Crystals of **2**, well-formed small dark green prisms, suitable for X-ray diffraction were obtained by slow vapor diffusion of methanol into concentrated aqueous solutions of **2** at 5 °C.

Crystal data for **2**: C₂₀H₂₄Cu₂N₄Na₄O₂₀, M_r = 895.50, triclinic, space group P $\bar{1}$, a = 11.1489(15), b = 12.8545(9), c = 13.3454(19) Å, α = 63.855(8), β = 78.305(12), γ = 68.695(10)°, V = 1597.5(3) Å³, T = 293 K, Z = 2, ρ_{calcd} = 1.862 g cm^{−3}, $\mu(\text{MoK}\alpha)$ = 1.485 mm^{−1}. Lorentz and polarization effects and absorption correction. 5579 unique reflections, and 3616 observed with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS 97, and refined by the full-matrix least-squares method on F^2 using SHELXL 97. The hydrogen atoms from the organic ligand were located from a difference synthesis and refined with an overall isotropic thermal parameter, while those from the water molecules were not found or calculated. Refinement of 471 variables with anisotropic thermal parameters for all non-hydrogen atoms gave R = 0.0503 and R_w = 0.112, with S = 0.97. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157314. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Conjugated Complexes Composed of Quinonediimine and Palladium: Controlled Formation of a Conjugated Trimetallic Macrocycle**

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π -Conjugated polymers have attracted much attention for application as electrical materials owing to their electrical properties.^[1] The properties of π -conjugated polymers are considered to be modified drastically by the incorporation of metal atoms.^[2, 3] Conjugated polymeric complexes in which transition metals are incorporated in the main chain represent one approach.^[3] Most of the interest in these conjugated polymeric complexes has been concerned with the nature of the interactions between metal centers through a π -conjugated chain. Transition metal directed assembly is regarded as

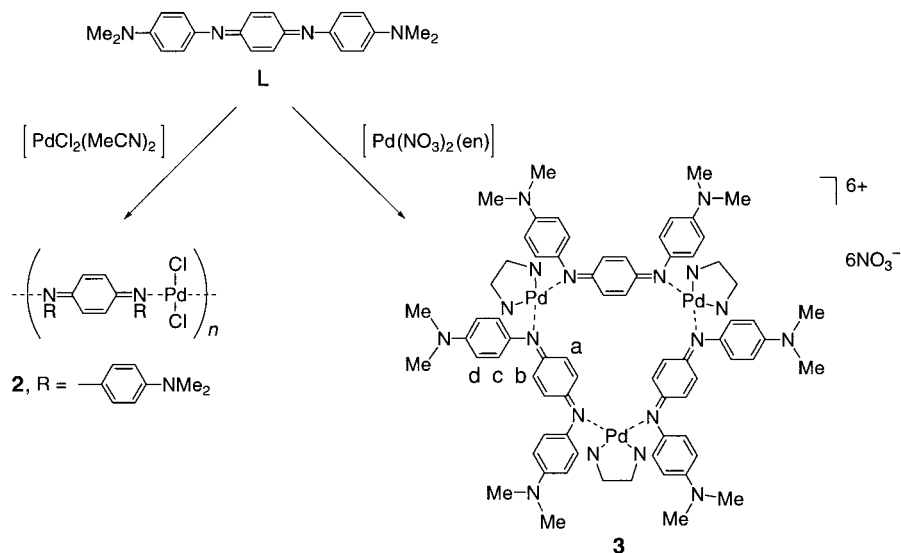
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a useful approach to an architecturally controlled formation of conjugated polymeric or macrocyclic complexes with π -conjugated ligands.^[4] We have already demonstrated that the redox-active π -conjugated ligand *N,N'*-bis(4-dimethylamino-phenyl)-1,4-benzoquinonediimine (L) serves as a bridging ligand to afford the conjugated homobimetallic palladium(II) complex [L'PdLPdL'] (**1**) with the palladium(II) complex bearing the *N*-heterocyclic tridentate podand ligand *N,N'*-bis(2-phenylethyl)-2,6-pyridinedicarboxamide (L').^[5] Complex **1** is present as a mixture of *syn* and *anti* isomers in dichloromethane. An array of L with a palladium complex having two coordination sites was expected to give a conjugated polymeric or macrocyclic complex. In fact, control of the coordination mode of the quinonediimine moiety of L allowed the formation of a conjugated trimetallic macrocycle.

Treatment of L with [PdCl₂(MeCN)₂] in acetonitrile led to the formation of the conjugated polymeric complex **2**, in which palladium centers are incorporated in the main chain (Scheme 1). The electronic spectrum of **2** in DMSO exhibited



Scheme 1. Reaction of L with [PdCl₂(MeCN)₂] and [Pd(NO₃)₂(en)].

a strong, broad absorption around 600–1000 nm, probably assignable to a low-energy charge-transfer transition with significant contribution from palladium; this indicates the coordination of the quinonediimine nitrogen atoms to palladium centers.^[5] The broad absorption band supports the formation of the conjugated polymeric complex **2**.^[6] In **2**, both *syn* and *anti* configuration of the quinonediimine moieties appear to be present.

To regulate the coordination mode of the quinonediimine moiety, a metal-directed strategy for the construction of metallomacrocycles was embarked upon by using [Pd(NO₃)₂(en)] which has *cis* binding sites as a “metal clip”. The conjugated trimetallic macrocycle [{Pd(en)(L)}₃](NO₃)₆ (**3**) was obtained quantitatively by treating L with an equimolar amount of [Pd(NO₃)₂(en)] (Scheme 1). The formation of the trimetallic macrocycle **3** was elucidated from spectral data. Only one well-resolved signal for each type of proton was observed in the downfield region of the ¹H NMR

spectrum (Figure 1); this indicates the formation of a symmetrical macrocycle. Furthermore, the H_a and H_b protons of the quinonediimine moiety were observed as singlet, which suggests the *syn* configuration. No other products were

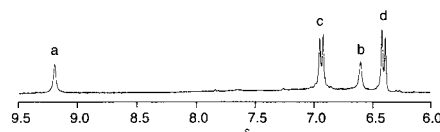


Figure 1. Downfield region of the ¹H NMR spectrum of **3**. For details see text.

detected. The ESI-MS spectrum also supported the formation of **3** (*m/z* 255.3 [*M* – 6NO₃]⁶⁺, 318.4 [*M* – 5NO₃]⁵⁺, 414.0 [*M* – 4NO₃]⁴⁺, 573.9 [*M* – 3NO₃]³⁺, 890.9 [*M* – 2NO₃]²⁺; Figure 2). The electronic spectrum of **3** in MeOH exhibited a strong, broad absorption band around 800 nm (Figure 3), probably assignable to a low-energy charge-transfer transition

with significant contribution from palladium owing to the coordination of the quinonediimine nitrogen atoms to palladium centers.

Further structural information on **3** was obtained by X-ray crystallography.^[7] The solid-state molecular structure of **3** confirmed a trimetallic macrocyclic skeleton and the coordination of both quinonediimine nitrogen atoms to the palladium centers in the *syn* configuration with a Pd–Pd distance of 7.68 Å (Figure 4). The molecule sits on an inversion center. The most noteworthy structural feature is that the quinonediimine planes are inclined at about 28° to the plane defined by the six nitrogen atoms of the quinonediimine moieties. An open cavity with different faces is formed, which is

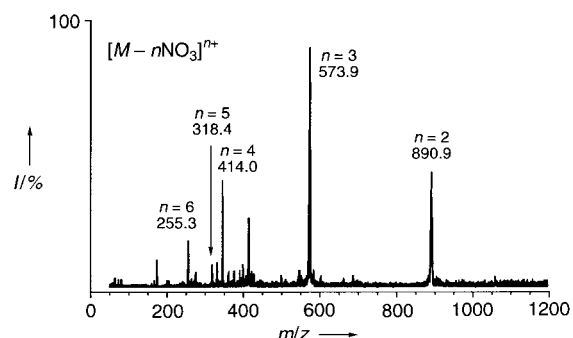


Figure 2. ESI-MS spectrum of **3**. *I* = intensity.

reminiscent of the cone conformation of calixarenes. This inclination of the quinonediimine planes is probably due to the coordination of the nitrogen atoms to the palladium centers, which results in ideal bite angles at Pd (N_{qd}–Pd–N_{qd} 91.2, 91.3°). The top and bottom sizes of the cavity, defined as

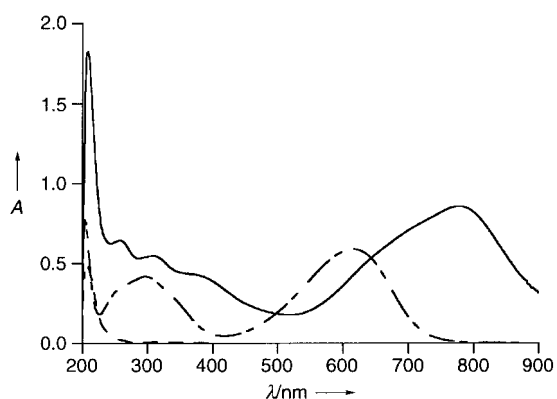


Figure 3. Electronic spectra of $[\text{Pd}(\text{NO}_3)_2(\text{en})]$ (----), **L** (— · —), and **3** (—); $2.0 \times 10^{-5} \text{ M}$ in MeOH. A = absorbance.

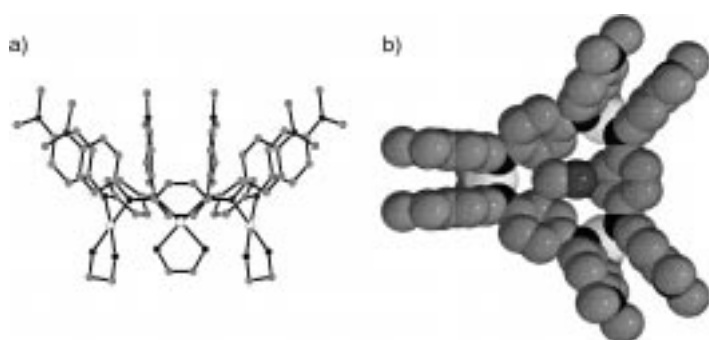


Figure 4. a) Molecular structure of **3** (H atoms, NO_3^- ions, and MeOH molecules omitted for clarity). b) Space-filling representation of the molecular structure of **3** (H atoms and NO_3^- ions omitted for clarity). Two MeOH molecules are located at the top and bottom of the cavity.

the distance between C_a and C_a' and between C_b and C_b' , are 3.66 and 6.72 Å, respectively (Figure 5). Due to π conjugation of **L**, the orientation of each phenylene ring should be nearly parallel to the quinonediimine plane. The steric interaction between the hydrogen atoms H_b and H_c , however, requires rotation of the phenylene ring of **L** away from this orientation, and results in dihedral angles of 43.2, 45.4, and 53.3° between the phenylene and quinonediimine planes (Figure 5). Another remarkable feature of the structure is the orientation of the phenylene rings of **L** in a face-to-face arrangement at a

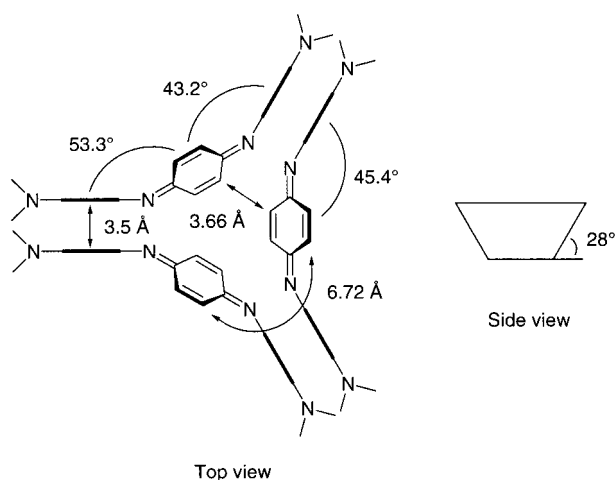


Figure 5. Schematic representation of **3**.

distance of about 3.5 Å at each corner of the triangle, which suggests a π - π stacking interaction. In addition to *cis* binding to $[\text{Pd}(\text{en})]$ units this π - π stacking interaction may partly contribute to the preferential formation of the trimetallic macrocycle over polymeric complexes. Architectural control of well-arranged metallomacrocycles based on transition metal directed assembly is a current research area in metal-directed chemistry.^[4, 8, 9] Considerable attention has been focused on the construction of a variety of metallosquares,^[4, 8] while metallotriangles have remained relatively unexplored.^[4c-e, 8h,m,o, 9] The angular strain at the metal center and the ligand flexibility resulted in the selective formation of the metallotriangle **3**.

Macrocycle **3** accommodates two MeOH molecules at the top and bottom of the cavity. This indicates the capability to encapsulate guest molecules. A preliminary experiment on guest binding in D_2O showed that the association constant for 1,2-dimethoxybenzene, calculated from ^1H NMR spectroscopic data, was $4.0 \times 10^3 \text{ M}^{-1}$.

In conclusion, an alternative coordination array of the redox-active π -conjugated bridging quinonediimine spacer **L** and a palladium unit led to the formation of the conjugated polymeric complex **2** or the conjugated trimetallic macrocycle **3**. In the latter case, the complexation is architecturally controlled by *cis* binding to $[\text{Pd}(\text{en})]$ fragments to give a trimetallic macrocycle with a cone conformation. A π - π stacking interaction between the phenylene rings of **L** may stabilize the triangular complex. An open cavity appears to offer a binding site for guest molecules. The present conjugated complexes are regarded as potential redox-active systems, which might be applied as catalysts and electronic materials. Further investigation, including redox and recognition properties of the trimetallic macrocycle **3**, is now in progress.

Experimental Section

3: A mixture of **L** (69.0 mg, 0.20 mmol) and $[\text{Pd}(\text{NO}_3)_2(\text{en})]$ (58.1 mg, 0.20 mmol) was stirred in acetonitrile (20 mL) under argon at room temperature for 2 h. After evaporation of the solvent, compound **3** was isolated in 92% yield by recrystallization from methanol. ^1H NMR (400 MHz, D_2O): δ = 9.17 (s, 6H), 6.91 (d, J = 8.7 Hz, 12H), 6.58 (s, 6H), 6.37 (d, J = 8.7 Hz, 12H), 3.01–2.95 (m, 6H), 2.94–2.88 (m, 6H), 2.90 (s, 36H); ^{13}C NMR (100 MHz, D_2O): δ = 158.1, 151.7, 136.9, 134.5, 129.2, 127.1, 112.6, 47.0, 39.7; ESI-MS: see Figure 2.

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- [6] The distinct signal broadening observed by NMR spectroscopy during the titration of L with $[\text{PdCl}_2(\text{MeCN})_2]$ indicated the formation of a conjugated polymeric complex. We have also demonstrated that the controlled complexation of the emeraldine base of poly(*o*-toluidine) with Pd^{II} compounds in an organic solvent affords cross-linked conjugated polymeric complexes.^[2b]
- [7] Crystal data for **3**: $\text{C}_{72}\text{H}_{96}\text{N}_{24}\text{O}_{18}\text{Pd}_3 \cdot 2\text{CH}_3\text{OH}$, $M_r = 1968.98$, orthorhombic, space group $Pnma$ (no. 62), $a = 27.6315(9)$, $b = 22.1045(7)$, $c = 17.7133(6)$ Å, $V = 10818.9(6)$ Å³, $Z = 4$, $T = 23.0^\circ\text{C}$, $\rho_{\text{calcd}} = 1.209$ g cm⁻³, $\mu(\text{MoK}\alpha) = 5.59$ cm⁻¹, $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å), $R = 0.090$, $R_w = 0.253$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160516. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Directing Topoisomerase I Mediated DNA Cleavage to Specific Sites by Camptothecin Tethered to Minor- and Major-Groove Ligands**

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Hairpin polyamides containing pyrrole- and imidazole-carboxamide units represent convenient tools to target specific sequences in DNA.^[1] These compounds form dimeric motifs that fit snugly into the minor groove of B-DNA and recognize defined sequences through the formation of an array of hydrogen bonds and van der Waals contacts. They provide a paradigm for the design of small molecules that regulate genes.^[2]

The sequence-recognition properties of hairpin polyamides can be exploited for directing DNA-cleaving and -alkylating agents to particular sequences.^[3–7] By analogy, we reasoned that they could also be used to direct the action of DNA-cleaving proteins such as topoisomerases. These ubiquitous

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