

Facile synthesis of multinuclear complexes based on a tetra(4-pyridyl)amidinate dirhodium(II) dimer†

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Received (in Cambridge, UK) 3rd October 2007, Accepted 20th November 2007

First published as an Advance Article on the web 13th December 2007

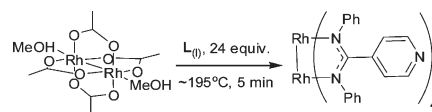
DOI: 10.1039/b715205a

Four rhenium(I) chromophores attached to a dirhodium(II) core form a new hexametallal light-harvesting assembly as characterised by X-ray crystallography, UV-vis spectroscopy and electrochemistry.

Considerable attention has focussed on the photochemistry and photophysics of metal complexes, such as Ru(II) and Re(I) polypyridyl complexes, over the past twenty years.¹ The interest in these compounds stems from their accessible, long-lived metal-to-ligand charge transfer (MLCT) excited state at room temperature.² Although the properties of these photosensitizers, *e.g.* their absorption and emission energies, can be fine-tuned by varying the polypyridyl ligands bonded to the metal ions,³ their efficiency as photosensitizers remains low if they are used as mononuclear complexes. The overall effectiveness of a photovoltaic or photocatalytic system should increase when multiple chromophores are all linked to one central reaction centre,⁴ in a way reminiscent of the light-harvesting complexes of natural photosystems.⁵

One approach to the assembly of light-harvesting polynuclear complexes is to attach chromophores to the paddlewheel motif of metal dimers. For example, four Ru(II)-based chromophores were bound to a tetraacetate rhodium dimer through the displacement of the acetates.⁶ Although not a self-assembly process, this method proved more facile than building up polynuclear complexes by axial coordination of metal tetracarboxylate dimers, as only two complexes can bind to the axial sites at a time.⁷ A drawback of this approach, however, is the limited stability of the complexes in solution due to subsequent chromophore displacement. Amidinate ligands may be used to increase the stability of the dimetallic core, however, the amidinates are less easily displaced in order to build up polynuclear complexes. An alternative approach, presented herein, is to functionalize the amidinate ligands to allow the attachment of photosensitizers while maintaining the tetraamidinate metal dimer as the central core. This approach will offer four points of attachment to the standard paddlewheel motif without requiring further ligand displacement reactions. To this end, the new tetra(*N,N'*-diphenylisonicotinamidinate) dirhodium(II) dimer (**1**) was synthesized and then allowed to react with a rhenium(I) bipyridine tricarbonyl complex, forming the tetra-Re(I)-[Rh(II)₂] dimer complex (**2**) through simple coordination chemistry.

The ligand *N,N'*-diphenylisonicotinamidinate (**L**) was synthesized following literature techniques.⁸ Two key features of this ligand are



Scheme 1 Synthesis of complex 1.

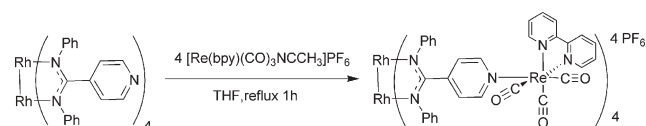
important for the formation of the dimer: it possesses a pyridyl group available for metal ion coordination and it has bulky phenyl rings that will encumber the axial site of the dimer and thus possible self-polymerisation by axial pyridine coordination.⁹

The tetraamidinate complex (**1**) was synthesized by a melt reaction (Scheme 1). After purification, **1** was obtained as a red solid in modest yield (15%). The [Re(bpy)(CO)₃]₄(L)₄Rh₂(PF₆)₄ complex (**2**) was synthesized by adapting known pyridine coordination chemistry using (L)₄Rh₂ and [Re(bpy)(CO)₃-(NCCH₃)]PF₆ (Scheme 2),¹⁰ which gave **2** in a yield of 60%.†

Single crystals suitable for X-ray crystallography were obtained by vapour diffusion of water into a solution of **1** in DMSO and by vapour diffusion of diisopropyl ether into a solution of **2** in acetonitrile.‡ It is notable that both complexes form chiral compounds in the solid state due to the packing of the phenyl rings. It is interesting to note that while **1** is a racemic mixture in the solid state, **2** forms enantiomerically pure single crystals with racemic twinning (Fig. 1b and 2b).

The structure of **1** is very similar to tetra(*N,N'*-diphenylbenzamidate) rhodium dimer, Rh₂(dpb)₄ (**3**), only with a slightly longer Rh–Rh bond length (Table 1).⁹ The packing of **1** is relatively loose, with only one water molecule forming hydrogen-bond interactions between two pyridyl moieties, and with the DMSO molecules occupying the free space between the dimers.

The structure of **2**–CH₃CN features the first crystallized acetonitrile mono-adduct bonded axially to a tetra(*N,N'*-diphenyl-arylaminidate) (Fig. 2). The present structure can be compared to the tetra(*N,N'*-diphenylformamidate)Rh₂ dimer, Rh₂(dpf)₄ (**4**), and the CO mono-adduct of Rh₂(dpb)₄ which exhibit more equivalent steric encumbrance to **2**–CH₃CN.^{9,11} In all cases, acetonitrile bis-adducts have never previously been reported. The acetonitrile forms a slightly longer bond to the rhodium compared to Rh₂(dpf)₄ in **4**–CH₃CN, an indication of the higher steric constraints in **1**. As reported in Table 1, the Rh–Rh distance is



Scheme 2 Synthesis of complex 2.

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† Electronic supplementary information (ESI) available: General methods for the synthesis of compounds **1** and **2** with NMR and High-Res mass spectrometry data. See DOI: 10.1039/b715205a

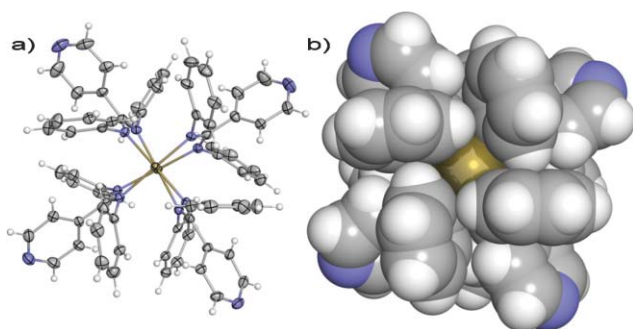


Fig. 1 Crystal structure of **1** viewed along the Rh–Rh axis: (a) ORTEP⁸ view with 50% probability ellipsoids; (b) space-filling model showing the helix formed by the phenyl rings of one of the enantiomers. Five dimethyl sulfoxides, two water molecules and a second dimer present in the asymmetric unit have been omitted for the sake of clarity.

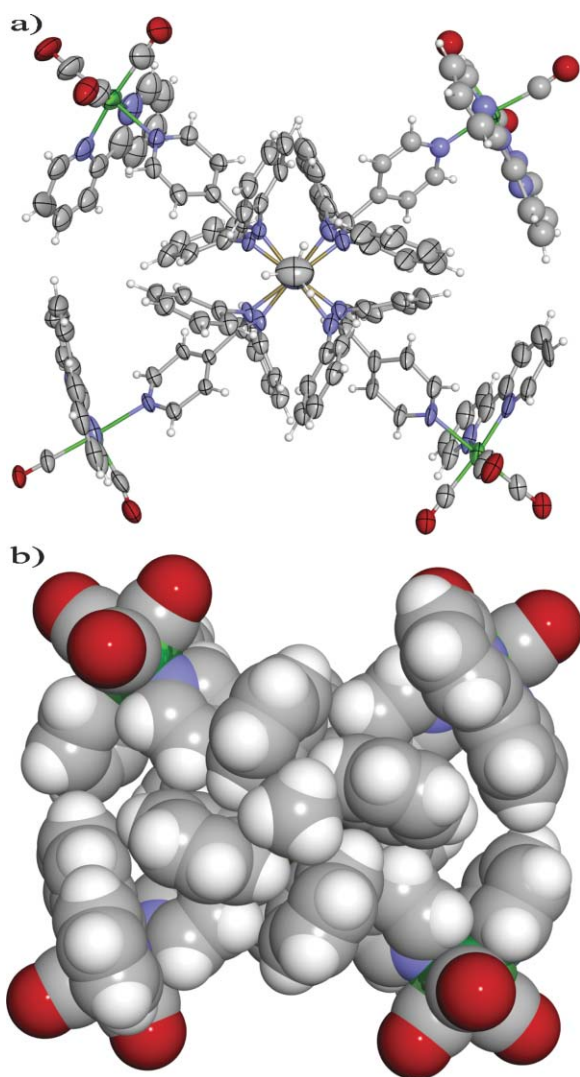


Fig. 2 Crystal structure of **2-CH₃CN** viewed along the Rh–Rh axis: (a) ORTEP⁸ view with 30% probability ellipsoids; (b) space filling model showing the clockwise helix formed by the phenyl rings. Four PF₆ anions and two acetonitrile molecules have been omitted for the sake of clarity.

Table 1 Selected parameters (Å and °) for **1**, **2** and related complexes

Lengths	1	2-CH₃CN	3^a	4^b	4-CH₃CN^b
Rh–Rh	2.4055(8)	2.414(3)	2.389(1)	2.457(1)	2.459(1)
Rh–N ^c	2.054(9)	2.06(1)	2.05(6)	2.057(1)	2.062(2)
Rh–N ^d		2.09(3)			2.066(2)
Rh–N _{adduct}		2.17(3)			2.106(4)
Torsion angle					
N–Rh–Rh–N'	12.6(4)	14.6(6)	17.3	3.5	16.8

^a **3**: Rh₂(diphenylbenzamidate)₄ ref. 9. ^b **4**: Rh₂(diphenylformamidate)₄ ref. 11. ^c On the Rh without adduct. ^d On the Rh with adduct.

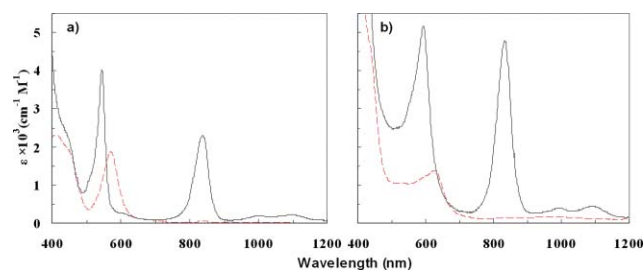


Fig. 3 Absorption spectra of (a) complex **1** in CHCl₃ (black full line) and in CH₃CN (red dashed line); (b) complex **2** in acetone (black full line) and in CH₃CN (red dashed line).

almost unaffected by the acetonitrile adduct, which is in line with that observed for Rh₂(dpf)₄ and its acetonitrile mono-adduct. In contrast, the CO mono-adduct of Rh₂(dpb)₄ showed a more distinct increase in its Rh–Rh bond length (0.046 Å) due to the π backbonding of the rhodium dimer to CO.

There is a 2° increase in the N–Rh–Rh–N torsion angle between **1** and **2-CH₃CN**. In comparison, the N–Rh–Rh–N torsion angle in the Rh₂(dpf)₄ dimer passed from 3.5° to 16.8° upon formation of the acetonitrile adduct,¹¹ but the more similar Rh₂(dpb)₄ didn't show any significant change upon CO adduct formation.⁹

No significant changes to bond lengths and angles are found for the rhenium motifs bonded to the central Rh–Rh dimer. All of the carbonyl bonds have very similar *facial* coordination environments. The crystal packing of **2-CH₃CN** shows some head-to-tail π stacking interactions between the bipyridines and phenyl rings and carbonyl–carbonyl interactions in the *a-b* plane. The PF₆ anions and acetonitrile solvent of crystallisation occupy the space near the rhenium moieties.

UV-vis absorption spectra of **1** and **2** are shown in Fig. 3 and their data are collected in Table 2. The complexes display high absorption in the UV region near 250 nm attributable to the aryl groups of the four coordinated amidinate ligands. The molar

Table 2 UV-vis absorption data of **L**, **1**, **2** and related complexes

Compound	Solvent	λ_{\max}/nm ($\epsilon \times 10^3/\text{M}^{-1} \text{cm}^{-1}$)
L	CH ₃ CN	254 (14.4)
1	CHCl ₃	255 (63) 433 (sh) (~2.5) 545 (4.0) 838 (2.1)
1	CH ₃ CN	267 (55) 415 (2.3) 571 (1.9) 839 (0.05)
2	Acetone	n.a. n.a. 592 (5.0) 832 (4.7)
2	CH ₃ CN	244 (120) 440 (sh) (~4.7) 626 (1.4)
Rh ₂ (dpb) ₄ ^a	Toluene	n.a. 440 (sh) 518 (6.1) 847 (2.9)
Rh ₂ (dpb) ₄ ^a	CH ₃ CN	n.a. 547

^a From ref. 9.

Table 3 Half-wave potentials for **1**, **2** and related compounds^a

Compound	$E_{1/2}/V$				
	Re ²⁺ / Re ¹⁺	Rh ₂ ⁶⁺ / Rh ₂ ⁵⁺	Rh ₂ ⁵⁺ / Rh ₂ ⁴⁺	Re ¹⁺ / Re ⁰	Rh ₂ ⁴⁺ / Rh ₂ ³⁺
1 ^b	—	1.24 (69)	0.21 (73)	—	−1.42 (88)
2 ^c	1.87 (142)	1.39 (97)	0.38 (83)	−1.17 (65)	−1.42 (89)
3 ^d	—	1.08	0.05	—	−1.52
5 ^e	1.75	—	—	−1.18	—

^a Potentials are in volts vs. SCE for acetonitrile solutions, 0.1 M in TBAP, recorded at 25 ± 1 °C. The difference between cathodic and anodic peak potentials (mV) is given in parentheses. ^b Sweep rate of 20 mV s^{−1}. ^c Sweep rate of 200 mV s^{−1}. ^d Rh₂(dpb)₄ from ref. 9. ^e 5: Re(bpy)(CO)₃(pyridine)PF₆ from ref. 12.

absorptivity in acetonitrile of this maximum almost quadruples for **1** compared to **L** and increases another two-fold for **2**, the higher absorptivity, in this case, coming from the additional bipyridine ligands. In the spectrum of **2** the MLCT absorption band due to the rhenium, expected near 360 nm as for Re(bpy)(CO)₃(pyridine)PF₆,¹² is masked by various ligand based transitions seen in both **1** and **2**.

The visible spectra of the complexes all exhibit absorptions due to the Rh₂ core and show very similar features to the known Rh₂(dpb)₄.⁹ Two strong absorption bands in **1** and **2** are found in non-coordinating solvents, at 545 and 838 nm, and 592 and 832 nm, respectively, with the latter being associated with a Rh₂(π*) → Rh₂(σ*) transition.¹³ The collapse of the latter in CH₃CN is due to the destabilisation of the σ* orbital by the axial adduct, with weaker bands observed at 571 and 626 nm.

The cyclic voltammogram of **1** (Table 3) shows a shift to more positive redox potentials as compared to Rh₂(dpb)₄ due to the pyridyl moieties that draw electron density away from the rhodium dimer. All of the expected redox processes are present in **2**. The three oxidation waves are all shifted to more positive potentials due to the 4⁺ formal charge of the complex, which increases the difficulty in its oxidation. The two reduction waves, however, are ligand-based and are not affected by the charge of the complex. The fact that there is only one oxidation process of higher intensity for the Re(I/II) oxidation is a clear sign of an absence of communication among the rhenium centres in **2**.

We have prepared a new tetraamidinate metal dimer which serves as a platform for the synthesis of multimetallic complexes. The rhenium centres bring their independent properties to the final assembled structure, and future work will probe their photo-physical properties in the new complex. The new multimetallic complex shows great potential for further coordination through its axial coordination site.

We are grateful to the Natural Sciences and Engineering Research Council of Canada, le Fonds québécois de la recherche sur la nature et les technologies (D. C.), the Centre for Self-Assembled Chemical Structures and the Université de Montréal

for financial support. We also thank Dr Michel Simard and Dr Frank Schaper for advice concerning the X-ray crystallography.

Notes and references

‡ Crystal data for **1**, (C₇₂H₅₆N₁₂Rh₂) 2.5(C₂H₆OS) (H₂O), were collected on a Bruker Microstar at 100(2) K using Cu-Kα radiation (λ = 1.54178 Å). Full-matrix, least squares refinements on F₂ using all data. 47610, *M* = 3016.89, monoclinic, space group *P*2₁/c, *a* = 25.6654(14), *b* = 27.3601(15), *c* = 21.9392(11) Å, α = 90.00, β = 113.913(3), γ = 90.00°, *U* = 14 083.4(13) Å³, *Z* = 8, *R*1 [*I* > 2σ(*I*)] = 0.0535, *wR*2 (all data) = 0.1548. CCDC 662537.

Crystal data for **2**, (C₁₂₆H₉₁N₂₁O₁₂Re₄Rh₂) 4(F₆P) 0.5(C₂H₃N), were collected on a Bruker Microstar at 100(2) K using Cu-Kα radiation (λ = 1.54178 Å). Full-matrix, least squares refinements on F₂ using all data. 23443, *M* = 3703.81, orthorhombic, space group *P*2₁2₁2₁, *a* = 20.3501(10), *b* = 26.4964(15), *c* = 26.9640(19) Å, α = 90.00, β = 90.00, γ = 90.00°, *U* = 14 539.1(15) Å³, *Z* = 4, *R*1 [*I* > 2σ(*I*)] = 0.1087, *wR*2 (all data) = 0.3030, Flack parameter = 0.38(3). CCDC 662536. Using the Squeeze algorithm of Platon to remove disordered solvent and anions resulted in a drop in the structure factor to: *R*1 = 0.0787 and *wR*2 = 0.2210. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b715205a

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