Preliminary communication

Rapid assembly of rigid rods by metal complexation of bis(terpyridyl) ligands

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Abstract

The synthesis of rigid rods by a route involving alternating metal and bis(terpyridyl) ligand addition steps is described; and when combined with a final convergent step, this strategy rapidly produces species containing multiple metal centers. © 1999 Elsevier Science S.A. All rights reserved.

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The development of nanometer-sized molecules has attracted widespread interest [1,2] and has become an important goal for a number of advanced technologies. In particular, rigid rods of defined lengths have been identified as significant molecular ensembles that are useful for a variety of purposes. For example, they may function as machinery components such as axles [3]; or, when composed of conjugated subunits, they may be used as nanowires [4].

Such nano-architecture requires readily-available building blocks with well-defined structures and properties. These should allow for the modular stepwise construction of components and have the potential for one-step assembly; and they should be stable to heat and air. Many metal complexes are well-suited to this application, because of their ability to undergo facile ligand exchange under controlled conditions and because of the regular geometries (octahedral, tetrahedral,

etc.). Metal–amine complexes, particularly those employing aromatic ligands, exhibit all of the aforementioned traits; therefore, we have begun to investigate the assembly of rigid one-dimensional molecules [5] via complexation of terpyridyl ligands by ruthenium. An additional advantage of employing bis(terpyridyl)–metal complexes is their photo- and electrochemical behavior [5], which encourages their use in molecular wires and as components of models for light-harvesting systems in solar energy applications [6]. As such, arrays of redox-active centers have generated much excitement [7] because of their facile synthesis and novel physical properties.

Our initial studies on the preparation of monodisperse rigid rods has focused on metal complexation of multidentate ligands. The bis(terpyridyl) compound **2** [9] is an ideal organic building block because it is easily synthesized in large quantities and because it exhibits the desired complexation behavior to produce bimetallic species [3]. The general strategy is based on alternating metal and ligand addition steps (see Section 1) as shown in Scheme 1. Treatment of the ruthenium complex **1** [10] with the ligand **2**, followed by precipitation and counterion exchange with ammonium hexa-

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Scheme 1.

fluorophosphate furnished the compound **3** [11] quantitatively. Subsequent treatment with RuCl$_3$·3H$_2$O gave the bimetallic complex **4**, which was lengthened in a stepwise manner by alternating these two procedures, eventually yielding the trimetallic species **7**, which is ready for further elongation. Although the yields for the addition of ligand **2** to polymetallic species such as **7** decrease with increasing chain length, large amounts of this latter compound are produced in 25% overall yield for the five step sequence. To increase the efficiency of the synthesis, a final convergent step was employed. Thus, treatment of RuCl$_2$(DMSO)$_4$ [12] with two equivalents of complex **7** gave the heptametallic species **8** in a 21% overall yield; however, mass spectrometry (*vide infra*) indicated that the counterion exchange did not proceed to completion.

Because of the poor solubility of these complexes in common solvents, characterization proved challenging. To obtain ^{1}H-NMR data, it was necessary to employ a 10:3:0.2 mixture of CD$_3$CN/D$_2$O/KNO$_3$ (saturated solution in D$_2$O). Fortunately, the triplet corresponding to the hydrogen at the 4′ position of the middle ring of the terminal mono(terpyridyl) ligand did not overlap with any other signals; and its integration relative to that of the rest of the aromatic region could be used to confirm the quantity of incorporated bis(terpyridyl) ligands, although definitive assignments for the other hydrogens could not be made.

Ultimately, electrospray ionization mass spectrometry provided the most useful information, as has been observed for the confirmation of the structures of other polynuclear metal complexes [8]. For example, the spectrum of the heptametallic complex **8** was obtained directly from its acetonitrile solution. The base peak at $m/z = 749$ is assigned to a species with a net charge of $+7$ (M $- 9$PF$_6^-$ + HPO$_4^{2-}$). Interestingly, peaks were observed at $m/z = 1645$ and 1217, corresponding to M $- 14$PF$_6^-$ + 5HPO$_4^{2-}$ + Cl$^-$ and M $- 14$PF$_6^-$ + 3HPO$_4^{2-}$ + Cl$^-$ + POF$_4^-$, respectively, indicating that the counterion exchange was not complete. The apparent hydrolysis of PF$_6^-$ to HPO$_4^{2-}$ has been seen previously for complexes of ruthenium [8] and other transition metals [13], but it was reported to be unknown whether this occurs under the conditions of the isolation procedures or the mass spectral analysis. Combustion analyses (*vide infra*) of our complexes indicate that the isolation procedure does not cause the hydrolysis, the amount of which correlates to the amount of time elapsed between preparation of solutions for mass spectral analysis and the analysis itself. Additionally, the selective retention of the dianion HPO$_4^{2-}$ over the monoanion PF$_6^-$ has also been documented [8].

Interestingly, no dramatic changes are observed in the UV–visible spectra upon increasing chain length; however, there is a general trend in the longest wave-

length absorbance. Both the absorbance and the wavelength increase by small amounts on going from **4** to **5** to **6** to **7**: from λ_{max} (log ε) = 488 (4.41) to 495 (4.80) to 496 (4.89) to 499 (4.99), respectively.

In summary, the preparation of rigid rods containing up to seven metal centers has been accomplished. Current work is directed towards the preparation of higher oligomers, as well as the investigation of the physical properties of these novel molecules.

1. Experimental procedures and spectral data

(a) Bimetallic compound **4**·5H$_2$O: Complex **3** (1.22 g, 1.05 mmol), RuCl$_3$·3H$_2$O (274.5 mg, 1.05 mmol) and anhydrous ethanol (130 ml) were brought to reflux under argon. Heating was discontinued after 48 h; and upon cooling, a dark purple precipitate was formed. This was isolated by vacuum filtration, washed with ethanol and ether, and dried to yield 1.48 g (97%) of a dark powder, m.p. > 400°C; UV–vis (CH$_3$CN/H$_2$O/KNO$_3$) λ_{max} (log ε) 274 (4.75), 282 (4.75), 309 (4.87), 488 (4.41) nm; IR (KBr) 3423, 3062, 2923, 1603, 1449, 1406, 1388, 1285, 1247, 1162, 1123, 1084, 1029, 846, 779, 754, 698, 558, 483 cm^{-1}; ^{1}H-NMR (270 MHz, CD$_3$CN/D$_2$O/KNO$_3$) δ 9.20 (br s, 2H), 8.80 (d, J = 8.1 Hz, 4H), 8.70–8.76 (m, 4H), 8.52–8.58 (m, 4H), 8.42 (t, J = 8.1 Hz, 1H), 7.88–8.03 (m, 8H), 7.37–7.46 (m, 6H), 7.14–7.26 (m, 6H). Anal. Calc. for C$_{51}$H$_{45}$Cl$_3$F$_{12}$N$_9$O$_5$P$_2$Ru$_2$: C, 41.88; H, 3.10; N, 8.62. Found: C, 42.08; H, 3.47; N, 8.61.

(b) Complex **5**: Compound **4** (1.00 g, 0.729 mmol), ligand **2** (473.1 mg, 0.875 mmol), and methanol (85 ml) were brought to reflux under argon and kept there for 18 h. After cooling, the mixture was filtered through celite; and the filtrate was treated with NH$_4$PF$_6$ (612.8 mg, 3.76 mmol). The dark precipitate was collected by vacuum filtration and was dried to yield 1.26 mg (82%) of a reddish–purple solid, m.p. 260°C (dec.); UV–vis (CH$_3$CN/H$_2$O/KNO$_3$) λ_{max} (log ε) 275 (5.09), 285 (5.12), 314 (5.23), 495 (4.80) nm; IR (KBr) 3415, 3062, 1963, 1603, 1466, 1449, 1432, 1403, 1286, 1246, 1163, 1086, 1029, 845 cm^{-1}; ESI-MS m/z (rel. intensity, assignment) 903 (20, M − 2PF$_6^-$), 554 (14, M − 3PF$_6^-$), 452 (31, M − 2PF$_6^-$ + 2H$^+$), 379 (20, M − 4PF$_6^-$); ^{1}H-NMR (270 MHz, CD$_3$CN/D$_2$O/KNO$_3$) δ 9.19 (br s, 2H), 8.80 (d, J = 7.7 Hz, 6H), 8.69–8.76 (m, 6H), 8.55 (br s, 4H), 8.53 (d, J = 9.4 Hz, 2H), 8.41 (t, J = 8.1 Hz, 1H), 7.84–8.06 (m, 16H), 7.36–7.48 (m, 10H), 7.12–7.23 (m, 12H). Anal. Calc. for C$_{87}$H$_{59}$F$_{24}$N$_{15}$P$_4$Ru$_2$: C, 49.84; H, 2.84: N, 10.02. Found: C, 49.47; H, 3.16; N, 9.71.

(c) Trimetallic species **6**·9H$_2$O was prepared in 94% by a procedure similar to that described in part (a), above, to yield a dark red solid, m.p. > 400°C; UV–vis (CH$_3$CN/H$_2$O/KNO$_3$) λ_{max} (log ε) 244 (5.04), 276 (5.16), 308 (5.31), 496 (4.89); IR (KBr) 3414, 3055, 1952, 1603, 1465, 1448, 1431, 1402, 1285, 1247, 1084, 1029, 746, 483 cm^{-1}; ESI-MS m/z (rel. intensity, assignment) 710 (6, M − 4PF$_6^-$ − 3Cl$^-$ + 4POF$_4^-$ + H$_2$O), 604 (6, M − 4PF$_6^-$ − 3Cl$^-$ + 3H$_2$O), 445 (8, M − 4PF$_6^-$ + 3H$_2$O), 437 (10, M − 4PF$_6^-$ − 2Cl$^-$ + HPO$_4^{2-}$), 431 (11, M − 4PF$_6^-$), 303 (100, M − 4PF$_6^-$ − 2Cl$^-$ + 3H$_2$O); ^{1}H-NMR (270 MHz, CD$_3$CN/D$_2$O/KNO$_3$) δ 9.21 (s, 4H), 8.80 (d, J = 7.7 Hz, 6H), 8.70–8.76 (m, 6H), 8.56 (br s, 4H), 8.53 (d, J = 8.5 Hz, 2H), 8.41 (t, J = 8.2 Hz, 1H), 7.84–8.05 (m, 16H), 7.45 (d, J = 9.1 Hz, 4H), 7.38 (d, J = 5.7 Hz, 4H), 7.14–7.24 (m, 12H). Anal. Calc. for C$_{87}$H$_{77}$Cl$_3$F$_{24}$N$_{15}$O$_9$P$_4$Ru$_3$: C, 42.37; H, 3.15; N, 8.52. Found: C, 42.00; H, 3.55; N, 8.56.

(d) Complex **7** was synthesized by a method similar to that described in part (b), above, to give a 33% yield of a reddish–black powder; UV–vis (CH$_3$CN/H$_2$O/KNO$_3$) λ_{max} (log ε) 288 (5.34), 308 (5.41), 499 (4.99); ESI-MS m/z (rel. intensity, assignment) 1367 (21, M − 5PF$_6^-$ + 3HPO$_5^-$), 1324 (32, M − 6PF$_6^-$ + 2HPO$_5^-$ + 2PO$_2$F$_2^-$), 590 (100, M − 6PF$_6^-$ + 2PO$_2$F$_2^-$), 564 (68, M − 6PF$_6^-$ + HPO$_4^{2-}$); ^{1}H-NMR (270 MHz, CD$_3$CN/D$_2$O/KNO$_3$) δ 9.24 (s, 4H), 8.88 (d, J = 8.2 Hz, 8H), 8.79 (d, J = 8.4 Hz, 8H), 8.58–8.68 (m overlapping s, 12H), 8.49 (t, J = 8.1 Hz, 1H), 7.94–8.13 (m, 18H), 7.52 (br d, J = 5.7 Hz, 8H), 7.45 (br d, J = 5.7 Hz, 8H), 7.22–7.32 (m, 16H). Anal. Calc. for C$_{123}$H$_{83}$F$_{36}$N$_{21}$P$_6$Ru$_3$: C, 48.78; H, 2.76; N, 9.71. Found: C, 48.38; H, 3.11; N, 9.39.

(e) Preparation of **8**: complex **7** (125.5 mg, 0.0414 mmol), RuCl$_2$(DMSO)$_4$ (10.0 mg, 0.207 mmol), acetone (2.2 ml), and water (6 ml) were brought to reflux under an atmosphere of argon. After 19 h, the mixture was cooled to room temperature and was treated with NH$_4$PF$_6$ (67.5 mg, 0.414 mmol). The solution was concentrated to a volume of 10 ml, and the brick red precipitate was collected by vacuum filtration. The solid was dissolved in acetone and subjected to column chromatography on alumina with CH$_3$CN–H$_2$O–KNO$_3$ (sat. aq.) 10:3:0.2, followed by precipitation with NH$_4$PF$_6$ (134.6 mg, 0.826 mmol) to yield 114.5 mg of a highly insoluble dark red solid; ESI-MS m/z (rel. intensity, assignment) 1645 (6, M − 14PF$_6^-$ + 5HPO$_4^{2-}$ + Cl$^-$), 1217 (14, M − 14PF$_6^-$ + 3HPO$_4^{2-}$ + Cl$^-$ + POF$_4^-$), 749 (100, M − 7PF$_6^-$ + HPO$_4^{2-}$). Anal. Calc. for C$_{246}$H$_{166}$Cl$_2$F$_{72}$N$_{42}$P$_{12}$Ru$_7$: C, 47.43; H, 2.69; N, 9.55. Found: C, 47.84; H, 3.05; N, 9.18.

References

[1] For recent reviews, see: P.J. Stang, Chem. Eur. J. 4 (1998) 19; J.M. Tour, Chem. Rev. 96 (1996) 537.

[2] For selected examples, see: M. Altmann, V. Enkelmann, F. Beer, U.H.F. Bunz, Organometallics 15 (1996) 394; P. Kaszynski, A.C. Friedli, J. Michl, J. Am. Chem. Soc. 114 (1992) 601; H. Segawa, K. Kunimoto, K. Susumu, M. Taniguchi, T. Shimidzu, J. Am. Chem. Soc. 116 (1994) 11193; G.-X. Liu, R.J. Puddephatt, Organometallics 15 (1996) 5257.

[3] K.E. Drexler, Nanosystems, Molecular Machinery, Manufacturing, and Computation, Wiley, New York, 1992.

[4] S.F. Swallen, Z.-Y. Shi, W. Tan, Z. Xu, J.S. Moore, R. Kopelman, J. Lumin. 76 (1998) 193; L. Jones, II, J.S. Schumm, J.M. Tour, J. Org. Chem. 62 (1997) 1388, and references therein.

[5] J.-P Collin, P. Gavina, V. Heitz, J.-P. Sauvage, Eur. J. Inorg. Chem. 1 (1998).J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, Chem. Rev. 94 (1994) 993.

[6] K.T. Potts, D.A. Usifer, Macromolecules 21 (1988) 1985; M. Kaneko, A. Yamada, Adv. Polym. Sci. 55 (1984) 1.

[7] For examples see: S. Bodige, A.S. Torres, D.J. Maloney, D. Tate, G.R. Kinsel, A.K. Walker, F.M. MacDonnell, J. Am. Chem. Soc. 119 (1997) 10364, and references therein; H.A. Brison, T.P. Pollagi, T.C. Stoner, S.J. Geib, M.D. Hopkins, Chem. Commun. (1997) 1263; E.C. Constable, P. Harverson, Chem. Commun (1996) 33; S. Campagna, A. Giannetto, S. Serroni, G. Denti, S. Trusso, F. Mallamace, N. Micalli, J. Am. Chem. Soc. 117 (1995) 1754; S.S. Zhu, T.M. Swager, J. Am. Chem. Soc. 119 (1997) 12568.

[8] C. Moucheron, A. Kirsch-De Mesmaeker, A. Dupont-Gervais, E. Leize, A. Van Dorsselaer, J. Am. Chem. Soc. 118 (1996) 12834.

[9] F. Kröhnke, Synthesis 1 (1976).

[10] B.P. Sullivan, J.M. Calvert, T.J. Meyer, Inorg. Chem. 19 (1980) 1404.

[11] E.C. Constable, M.D. Ward, J. Chem. Soc. Dalton Trans. 1405 (1990).

[12] I.P. Evans, A. Spencer, G. Wilkinson, J. Chem. Soc. Dalton Trans. 204 (1973).

[13] R. Fernández-Galán, B.R. Marzano, A. Otero, M. Lanfranchi, M.A. Pellinghelli, Inorg. Chem. 33 (1994) 2309.