Observation of supramolecular π–π dimerization of a dinuclear ruthenium complex by ^{1}H NMR and ESMS

Eléna Ishow, André Gourdon* and Jean-Pierre Launay

Groupe Electronique Moléculaire, CEMES-CNRS, UPR 8011, BP 4347 29 Rue Jeanne Marvig, 31055 Toulouse, France. E-mail: gourdon@cemes.fr

The dinuclear ruthenium complex of bis{dipyrido[3,2-*f*:2′,3′-*h*]quinoxalo}[2,3-*e*:2′,3′-*l*]pyrene (bqpy) forms dimers in solution maintained only by π–π stacking of the bridging ligand, stable enough to be observed not only by ^{1}H NMR spectroscopy but also by electrospray mass spectrometry at low accelerating cone voltage.

In recent years much attention has been drawn to supramolecular architectures maintained by weak interactions.[1] We report here the first evidence, by ^{1}H NMR and electrospray mass spectrometry, of the supramolecular dimerization of a dinuclear metallic complex only maintained by π-π stacking.

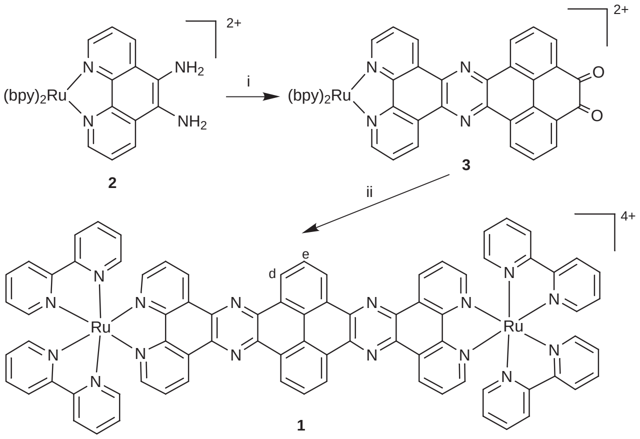
We have recently observed by ^{1}H NMR spectroscopy the supramolecular aggregation in solution of the monometallic complex $[(bpy)_2Ru(tpphz)]^{2+}$ where tpphz is the fully aromatic tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2‴,3‴-*j*]phenazine.[2] This dimerization by π–π stacking of the tpphz part, was not observed for the dinuclear complex $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$. Indeed, the relatively short intermolecular Ru–Ru distance (12.77 Å determined by X-ray diffraction), and therefore the high intermolecular coulombic repulsions, preclude any efficient stacking. Along these lines we have synthesized the dinuclear complex **1** of bis-{dipyrido[3,2-*f*:2′,3′-*h*]quinoxalo}[2,3-*e*:2′,3′-*l*]pyrene (bqpy). In this complex, the calculated intermetallic distance is *ca.* 20 Å, long enough to allow an efficient aggregation of two complexes.

Attempts to synthesize bqpy from 5,6-diamino-1,10-phenanthroline and tetraketopyrene[3] gave only intractable mixtures of insoluble bqpy and by-products. This lack of solubility emphasizes the very important π–π interactions in this type of compound. We have used instead the alternative synthetic route depicted in Scheme 1 which involves successive functionalizations of soluble precursor complexes.† Reaction of 6-amino-5-nitro-1,10-phenanthroline, obtained by nucleophilic amination of 5-nitro-1,10-phenanthroline,[2] with $Ru(bpy)_2Cl_2{\cdot}2H_2O$ in refluxing ethanol gave the corresponding amino–nitro complex in 82% yield which was then reduced by hydrazine hydrate over Pd/C to provide the diamino complex **2** in 89% yield. Condensation with tetraketopyrene[3] gave first **3** and then **1** on prolonged heating in acetonitrile–methanol–acetic acid (yield 64%). In contrast to the free ligand bqpy, **1** is soluble in various solvents depending on its counter anions.

As expected by analogy with the mononuclear $[(bpy)_2Ru(tpphz)]^{2+}$ complex, the ^{1}H NMR spectra are very sensitive to concentration.

On one hand, the bqpy protons are clearly the most affected with displacements up to 0.9 ppm between extreme conditions. Their signals are significantly broadened and move upfield with increasing concentration, the most influenced ones being the pyrene protons H^d and H^e; on the other hand, the bpy proton signals are only slightly broadened and move downfield in a smaller extent (maximum 0.1 ppm). We have attributed this concentration effect to the aggregation in solution of dinuclear species by π-stacking of the central bqpy aromatic parts. Consistent with this hypothesis, a temperature increase causes similar effects as dilution. This aggregation, which must be rapid with respect to the NMR timescale, modifies the local electron density and/or the ring current effects in the vicinity of the bqpy ligand. As a matter of fact, the π-stacking localizes the electron density on the central quinoxalopyrene part and decreases the electron density on the ruthenium atoms. These ^{1}H NMR spectra modifications are in agreement with those encountered in some host–guest organic complexes, catenanes and rotaxanes[4] in which inclusion induces shielding and broadening of the aromatic hosts and guest signals. The association constant monomer–dimer has been estimated at 830 M^{-1} by standard curve-fitting to a plot of chemical shift *vs.* concentration (at concentrations below 1.9×10^{-3} M).

This dimerization in solution can also be observed by electrospray mass spectrometry (ESMS). This soft ionisation method[5] has been recently used for the direct characterization of weakly bonded species containing non-covalent interactions such as receptor–ligand,[6] enzyme–substrate,[7] heme–protein complexes,[8] oligonucleotide duplexes[9] and hydrogen-bonded supramolecular assemblies.[10] Moreover, it has also been possible to observe by this technique the formation of multinuclear metal coordination complexes under equilibrium conditions.[11] As low ionisation energies are involved, non-covalent molecular architectures, the stability of which depends on weak interactions, are not destroyed so that ion distributions in the mass spectra reflect with confidence the species arrangement in solution. In our case, we have been able to isolate and discriminate the formation of the supramolecular dimer of **1** only maintained by weak π–π interactions by varying the accelerating cone voltage to control the fragmentation during the ionisation process. The ESMS spectrum recorded at cone voltage of 60 V showed four major peaks at *m/z* 1873, 864, 526 and 359.9 corresponding to pseudomonomolecular ions with the loss of 1, 2, 3, and 4 PF_6^-, and also a fifth intense peak at *m/z* 1200. A state of charge of **3**$^+$ was found for this peak by optimizing the resolution of the isotopic pattern. Both values, charge and mass unity, are in total agreement with the formation of the dimeric entity $\{[(bpy)_2Ru^{II}(bqpy)Ru^{II}(bpy)_2]_2 + 5PF_6^-\}^{3+}$ corresponding to a dimeric neutral



Scheme 1 *Reagents and conditions*: i, ii, tetraketopyrene, MeCN–MeOH–AcOH (20:15:1 v/v), reflux, 4 d, 64%

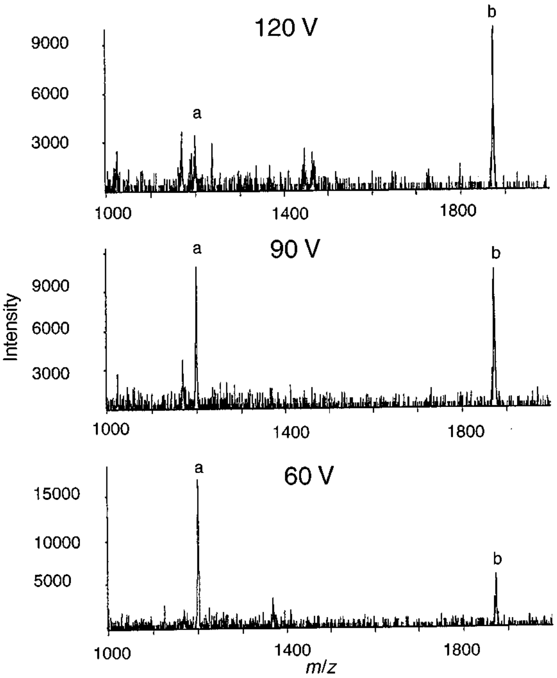


Fig. 1 Detail of the ESMS spectra of **1** in MeCN/H_2O 1 : 1 at cone voltages of 60, 90 and 120 V in the range *m/z* 1000–2000. a refers to the dimeric species $\{[\mathbf{1}_2](PF_6)_5\}^{3+}$ and b to the superimposition of the monomer $\{[\mathbf{1}](PF_6)_3\}^{+}$ and of the dimer $\{[\mathbf{1}_2](PF_6)_6\}^{2+}$. Note the scale change at 60 V.

species $\mathbf{1}_2$ after loss of three PF_6^- counter anions PF_6^-. And likewise, the peak at *m/z* 1873 is also clearly an isotopically resolved overlap of $\{\mathbf{1}\text{-}PF_6\}^+$ and $\{\mathbf{1}_2\text{-}2PF_6\}^{2+}$ species. Moreover, by raising the cone voltage to 90 and 120 V (Fig. 1), this peak intensity decreased and finally vanished, whereas the four other peaks remained nearly unchanged; simultaneously, the voltage increase engendered the partial fragmentation of the dinuclear complex **1** as a novel peak appeared at *m/z* 1169, assigned to the fragmentation product $[(bpy)_2Ru(bpqy)]^{2+}$ with one PF_6^-.

Although the exact geometry of this dimer in solution cannot be determined with accuracy by experimental techniques, some insights can be inferred from theories and experiments on small polyaromatic organic molecules and from molecular mechanics calculations. The steric crowding of the bulky $Ru^{II}(bpy)_2$ extremities imposes a geometry in which the metal–metal axes are more or less perpendicular to each other to allow a quite short bqpy–bqpy distance. In that conformation, both bqpy planes can be either perpendicular (T-shape) or parallel (stacked). On the basis on previous studies,[12] it seems reasonable to assume a stacked geometry for the dimer $\mathbf{1}_2$ in which the ligand bqpy exhibits a large aromatic extension. Stability of such stacked large systems actually results from a compromise between the dominant favourable van der Waals attraction, which seems to be linearly correlated with the number of aromatic moieties, and the repulsive coulombic interactions. In the case of the dimer $\mathbf{1}_2$, these repulsive coulombic interactions are considerably reduced by the strong electron-acceptor ruthenium extremities which decrease the electronic density on the central pyrene-type regions.[13] By positioning two complexes in this perpendicular conformation (Fig. 2), with the bqpy planes parallel at 3.5 Å, the distance between two ruthenium centres belonging to two different molecules is estimated to 14.5 Å which precludes any significant couloumbic repulsion between the metallic moieties.

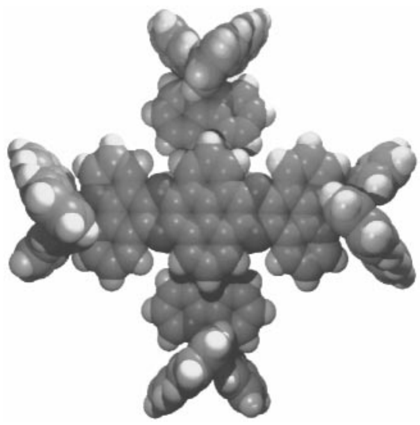


Fig. 2 CPK representation of the dimer $\mathbf{1}_2$

Additionally, such a geometry often exhibits an offset of the aromatic parts from the face-to-face aggregation for the stacked molecules to accommodate with the repulsive coulombic interactions allowed here by the length of the bridging ligand.

This work was supported by the CNRS and the EEC program Electron and Energy Transfer in Model Systems(CHRXCT-94-0538). S. Richelme and C. Claparols are acknowledged for ES–MS experiments.

Notes and References

† Spectroscopic data for **1**: ^{1}H NMR (Bruker WF250, 250 MHz, CD_3CN, 298 K, 2.6×10^{-4} M); δ 9.74 (d, *J* 7.0 Hz, 4H; H^d), 9.63 (d, *J* 8.2 Hz, 4H; H^c), 8.61 (d, *J* 8.3 Hz, 4H; H^3), 8.57 (d, *J* 8.5 Hz, 4H; H$^{3'}$), 8.38 (d, *J* = 7.0 Hz, 2H; H^e), 8.30 (dd, *J* 5.4, 1.3 Hz, 4H; H^a), 8.17 (ddd, *J* 8.0, 7.9, 1.4 Hz, 4H; H^4), 8.06 (ddd, *J* 8.0, 7.9, 1.4 Hz, 4H; H$^{4'}$), 7.99 (dd, *J* 8.2, 5.3 Hz, 4H; H^b), 7.92 (d, *J* 5.1 Hz, 4H; H^6), 7.82 (d, *J* 5.3 Hz, 4H; H$^{6'}$), 7.52 (ddd, J 6.5, 6.5, 1.2 Hz, 4H; H^5), 7.21 (ddd, J 6.2, 6.2, 1.2 Hz, 4H; H$^{5'}$); MS (ESMS, Perkin-Elmer Sciex, solvent: MeCN–H_2O (1:1 v/v), injection 5 µl min^{-1}); *m/z* 1873 $[M - PF_6^-]^+$, 864 $[M - 2PF_6^-]^{2+}$, 526 $[M - 3PF_6^-]^{3+}$, 359.9 $[M - 4PF_6^-]^{4+}$.

1 J.-M. Lehn, *Pure Appl. Chem.*, 1978, **50,** 871; *Supramolecular Chemistry*, VCH, Weinheim, 1995.
2 J. Bolger, A. Gourdon, E. Ishow and J.-P. Launay, *Inorg. Chem.*, 1996, **35**, 2937; *J. Chem. Soc., Chem. Commun.*, 1995, 1799.
3 H. Vollmann, H. Becker, M. Corell and H. Streeck, *Justus Liebigs Anal. Chem.*, 1937, **531**, 2.
4 See for example: D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154 and references therein; B. J. Whitlock and H. W. Whitlock, *J. Am. Chem. Soc.*, 1990, **112**, 3910.
5 M. Przybylski and M. O. Glocker, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 806 and references therein.
6 B. Ganem, Y.-T. Li and J. D. Henion, *J. Am. Chem. Soc.*, 1991, **113**, 6294.
7 M. Baca and S. B. Kent, *J. Am. Chem. Soc.*, 1992, **114**, 3992; B. Ganem, Y.-T. Li and J. D. Henion, *J. Am. Chem. Soc.*, 1991, **113**, 7818.
8 V. Katta and B. T. Chait, *J. Am. Chem. Soc.*, 1991, **113,** 8534.
9 B. Ganem, Y.-T. Li and J. D. Henion, *Tetrahedron Lett.*, 1993, **34**, 1445.
10 K. C. Russel, E. Leize, A. Van Dorsselaer and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 209.
11 E. Leize, A. Van Dorsselaer, R. Krämer and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1993, 990; A. Marquis-Rigault, A. Dupont-Gervais, P. N. W. Baxter, A. Van Dorsselaer and J.-M. Lehn, *Inorg. Chem.*, 1996, **35**, 2307 and references therein.
12 H.-J. Scheider, T. Schiestel and P. Zimmermann, *J. Am. Chem. Soc.*, 1992, **114**, 7698.
13 F. Cozzi, M. Cinquini, R. Annuziata and J. S. Siegel, *J. Am. Chem. Soc.*, 1993, **115**, 5330.

Received in Basel, Switzerland, 27th April 1998; Revised manuscript received 21st July 1998; 8/05809A