Dimers of delocalized Ru_3O clusters linked by *ortho*-metallated 2,2′-bipyrimidine in μ_4-η^1(C),η^1(C),η^2(N,N),η^2(N,N) mode†

Heng-Yun Ye, Li-Yi Zhang, Jing-Lin Chen and Zhong-Ning Chen*

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A remarkable cluster–cluster interaction is operative in dimers of delocalized $Ru_3O(OAc)_5(py)_2$ clusters with *ortho*-metallated 2,2′-bipyrimidine (bpym) in an unprecedented μ_4-η^1(C),η^1(C), η^2(N,N),η^2(N,N) bonding mode; interconversion of the dimeric species $[\{Ru_3O(OAc)_5(py)_2\}_2(\mu_4\text{-bpym})]^{n+}$ (n = 0, 1 or 2) with different charges is attainable by chemical oxidation or reduction.

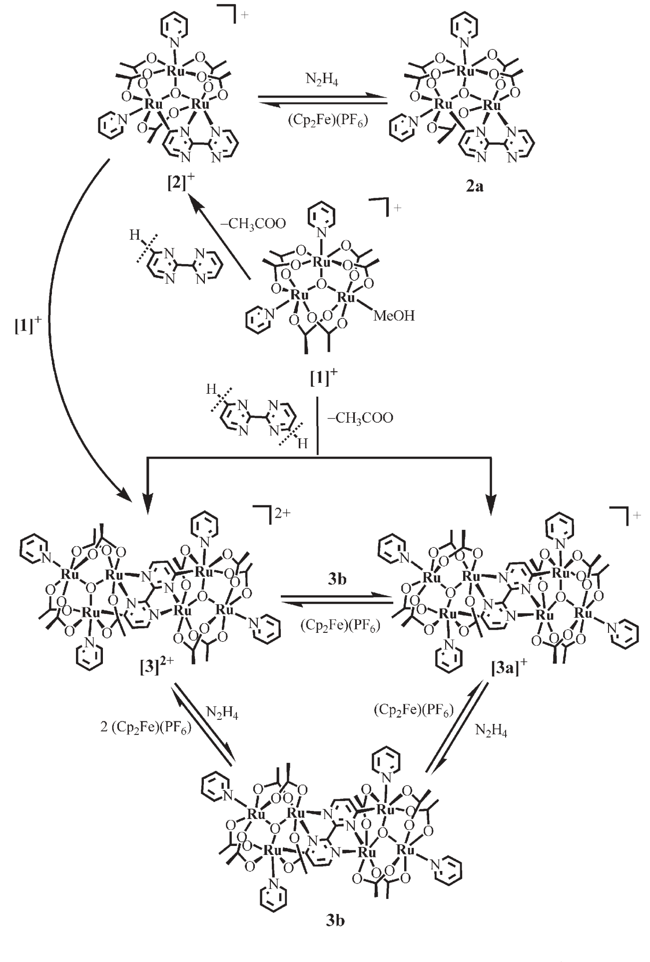
Ligand-mediated electronic interactions including electron/energy transfer between the metal centers are among the most remarkable features of multinuclear metal complexes with donor–spacer–acceptor assemblies.[1,2] While most of the electron or energy donors are mononuclear organometallic chromophores,[1,2] redox-active metal clusters with delocalized electronic structures have been comparatively neglected in the construction of donor–spacer–acceptor molecules because of the difficulty in controlling the ligand-bridged intercluster assembly.[3–7]

2,2′-Bipyrimidine (bpym) is a π-delocalized tetraimine ligand and has been utilized widely in the construction of polymetallic complexes that exhibit electronic or magnetic interactions.[8–15] The bis(bidentate) chelating character makes it serve as an excellent spacer to bring the metal centers into close proximity and create a pathway for electron/energy transfer[10,11,13] or magnetic coupling.[14,15] Its favorable efficiency in transmitting the electronic or magnetic interaction is ascribed to the ability to position two metal centers at a distance of *ca.* 5.5 Å in a fixed orientation which would allow a direct or indirect dπ–dπ interaction.

During our study of the reactivity of the oxo-centered triruthenium parent complex $[Ru_3O(OAc)_6(py)_2(CH_3OH)]^+$ ($[\mathbf{1}]^+$) with diimine,[16] we discovered that the *ortho* C–H bond in diimine can be activated and cleaved, giving oxo-centered triruthenium derivatives $[Ru_3O(OAc)_5(py)_2\{\mu\text{-}\eta^1(C),\eta^2(N,N)\text{-diimine}\}]^+$ by displacing one bridging acetate and axial methanol in the parent complex $[\mathbf{1}]^+$ through *ortho*-metallation of diimine. This finding prompted us to attempt cleavage of the *ortho* C–H bonds in tetraimine to attain dimers of delocalized Ru_3O clusters through double *ortho*-metallation of tetraimine.

We describe now that the deprotonated bpym serves as a monoanionic μ-η^1(C),η^2(N,N) or dianionic μ_4-η^1(C),η^1(C), η^2(N,N),η^2(N,N) ligand in the construction of tri- and hexanuclear ruthenium cluster complexes by single and double *ortho*-metallation, respectively.

As shown in Scheme 1, triruthenium derivative $[\mathbf{2}]^+$ was prepared by reaction of the parent triruthenium complex, $[\mathbf{1}]^+$,[17] with 1.5 equiv. of bpym. Reduction of $[\mathbf{2}]^+$ with excess aqueous hydrazine gave the one-electron reduced neutral compound **2a**. Reaction of bpym with 2.4 equiv. of $[\mathbf{1}]^+$, nevertheless, afforded dimeric complexes $[\mathbf{3}]^{2+}$ (dark blue) and $[\mathbf{3a}]^+$ (green) which were separated by alumina column chromatography. Intercluster mixed-valence complex $[\mathbf{3a}]^+$ ($[Ru_3^{III,III,II}\text{–bpym–}Ru_3^{III,III,III}]^+$) is most likely derived from $[\mathbf{3}]^{2+}$ ($[Ru_3^{III,III,III}\text{–bpym–}Ru_3^{III,III,III}]^{2+}$) by one-electron reduction during chromatographic separation. $[\mathbf{3}]^{2+}$ is also accessible by reaction of $[\mathbf{2}]^+$ with one equiv. of $[\mathbf{1}]^+$.



Scheme 1 Synthetic routes to Ru_3O cluster derivatives $[\mathbf{2}]^+$–**3b** with *ortho*-metallated bpym.

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. E-mail: czn@ms.fjirsm.ac.cn

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Addition of excess aqueous hydrazine to **[3]**$^{2+}$ or **[3a]**$^{+}$ afforded the neutral compound **3b** ($Ru_3^{III,III,II}$–bpym–$Ru_3^{III,III,II}$). Addition of **[3]**$^{2+}$ to one equiv. of **3b** also gave rise to isolable intercluster mixed-valence complex **[3a]**$^{+}$. It is intriguing that **[3]**$^{2+}$, **[3a]**$^{+}$ and **3b** could readily be interconverted by chemical oxidation or reduction. Addition of 1 or 2 equiv. of ferrocenium hexafluorophosphate could convert **3b** into **[3a]**$^{+}$ or **[3]**$^{2+}$ by oxidation. Oxidation of **[3a]**$^{+}$ by addition of one equiv. of ferrocenium hexafluorophosphate afforded **[3]**$^{2+}$.

Compounds **[2a]**(PF_6)–**3b** were characterized by microanalysis and spectroscopy (see ESI†), and by X-ray crystallography for compound **[3a]**(PF_6).‡ The microanalytical data accord well with the calculated values. The ESI-MS show $[M - (PF_6)_2]^{2+}$, $[M - (PF_6)]^{+}$ and $[M]^{+}$ as the principal peaks for **[3]**$(PF_6)_2$, **[2]**(PF_6) and **[3a]**(PF_6), and **2a** and **3b**, respectively.

As depicted in Fig. 1, the complex cation **[3a]**$^{+}$ consists of two triruthenium $Ru_3O(OAc)_5(py)_2$ clusters linked together by an *ortho*-metallated bpym with a twofold axis passing through the center of the C3–C3A bond linking the two pyrimidine rings. Formation of the $Ru_3O(OAc)_5(py)_2$ moiety is by replacement of one bridging acetate and one axial methanol in the original complex **[1]**$^{+}$ by *ortho*-metallated bpym. The dianionic bpym serves as a hexadentate ligand in an unprecedented μ_4-η^1(C),η^1(C),η^2(N,N),η^2(N,N) binding mode, bound to the ruthenium centers through its C and N donors in η^1- and η^2-coordination, respectively. The Ru–C and Ru–N bond lengths are comparable to those found in the triruthenium compound with *ortho*-metallated 2,2′-bipyridine.[16] The chelating η^2(N,N)-coordination is asymmetrical with the Ru1–N1 (1.974(9) Å) distance being obviously shorter than that of Ru1–N2 (2.113(9) Å).

The ruthenium centers exhibit distorted octahedral environments with N_2O_4, NO_5, and CNO_4 donors for Ru1, Ru2, and Ru3 atoms, respectively. The intracluster Ru–Ru (3.267(8)–3.375(9) Å) and Ru–O_{oxo} (1.907(7)–1.935(7) Å) distances are similar to those observed in other oxo-centered triruthenium cluster compounds.[18–21] The Ru–$O_{acetate}$ distances (2.026(9)–2.067(8) Å) are also in the normal ranges except for the one (Ru3–O12 = 2.186(9) Å) *trans*-oriented to the Ru3–C1 bond which is elongated significantly due to the remarkable *trans* effect induced by *ortho*-metallation of bpym. Triruthenium planes Ru1Ru2Ru3 and Ru1ARu2ARu3A, which are almost perpendicular to each other (dihedral angle = 89.2°), afford a dihedral angle of 44.6° with the bpym plane, respectively. The intercluster Ru···Ru separations across the bpym bridge are 5.42, 6.82, and 9.15 Å for Ru1···Ru1A, Ru1···Ru3A, and Ru3···Ru3A, respectively.

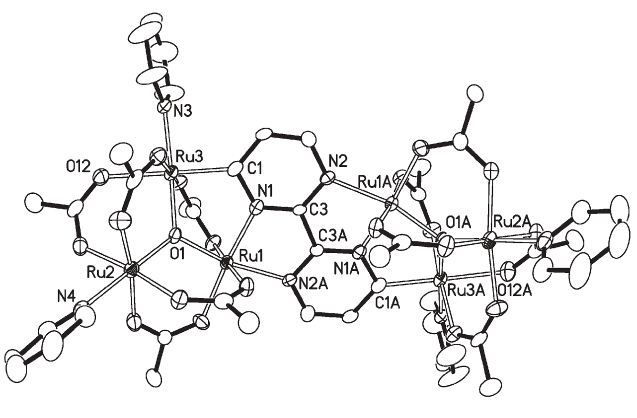

Fig. 1 ORTEP drawing of complex **[3a]**$^{+}$ with atom-labeling scheme showing 30% thermal ellipsoids.

As shown in Fig. 2, the triruthenium cluster derivatives **[2]**(PF_6) or its one-electron reduced form **2a** show three reversible redox waves at +0.75, −0.39 and −1.73 V in 0.1 M dichloromethane solution of tetrabutylammonium hexafluorophosphate, corresponding to the one-electron processes $Ru_3^{IV,III,III}/Ru_3^{III,III,III}$ (A), $Ru_3^{III,III,III}/Ru_3^{III,III,II}$ (B) and $Ru_3^{III,III,II}/Ru_3^{III,II,II}$ (C), respectively.[16,17] In the cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of dimeric compounds **[3]**$(PF_6)_2$, **[3a]**(PF_6) or **3b**, the corresponding redox waves A, B and C in individual Ru_3O cluster show obvious splitting due to cluster–cluster electronic interactions across the bpym bridge. The redox wave splitting can be estimated by the potential differences $\Delta E_{1/2}$ between $E^{A}_{1/2}$ and $E^{A'}_{1/2}$, $E^{B}_{1/2}$ and $E^{B'}_{1/2}$, and $E^{C}_{1/2}$ and $E^{C'}_{1/2}$, respectively. The values of $\Delta E^{A}_{1/2}$, $\Delta E^{B}_{1/2}$ and $\Delta E^{C}_{1/2}$ are 0.10, 0.23 and 0.25 V, corresponding to comproportionation constants,[22] K_c, of 49, 7730 and 16840, respectively. This demonstrates distinctly that intercluster interactions are dependent on the formal oxidation states of the Ru_3O cluster moiety and are in the order $Ru_3^{IV,III,III} < Ru_3^{III,III,III} < Ru_3^{III,III,II}$. It has been proposed that cluster–cluster interactions would occur through an orbital pathway with cluster–π*(ligand)–cluster mixing.[23–25] As the antibonding dπ*(Ru_3O) levels which are populated in the cathodic region are close in energy to the π*(bpym) levels, a more efficient cluster–cluster interaction would occur with an increase of the electron content in the Ru_3O cluster.

In the UV-vis-nIR spectra (Fig. 3), intense bands in the ultraviolet region are dominated by ligand-centered absorptions. The composite bands with intermediate energy (330–410 nm) are ascribable to cluster-to-ligand charge transfer (CLCT) transitions from the occupied dπ orbitals of the Ru_3O cluster to the lowest unoccupied π* orbitals of the ligands.[16,17,20] Relative to the band of **[2]**$^{+}$ at 330 nm, that of **2a** shifts to 380 nm. Likewise, the absorption energy of this band for the dimeric complexes is **[3]**$^{2+}$ (350 nm) > **[3a]**$^{+}$ (382 nm) > **3b** (404 nm). Consequently, this band is red-shifted with stepwise one-electron reduction of the Ru_3O cluster moieties because of the gradual raise of the energy levels of the dπ orbitals in the Ru_3O cluster.

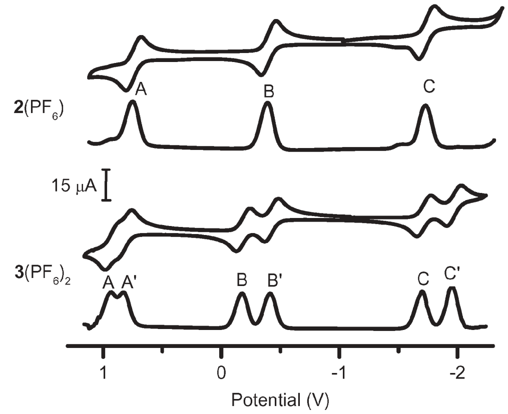

Fig. 2 Cyclic and differential pulse voltammograms (CV and DPV) of compounds **[2]**(PF_6) and **[3]**$(PF_6)_2$ in 0.1 M dichloromethane solution of $(Bu_4N)(PF_6)$. The scan rate is 100 mV s^{-1} for CV and 20 mV s^{-1} for DPV. Potentials in volts are referenced to Fc^+/Fc ($E_{1/2}$ = 0).

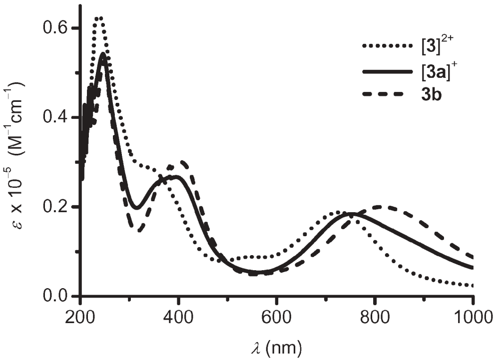

Fig. 3 UV-vis-nIR spectra of compounds [**3**](PF_6)$_2$ (dots), [**3a**](PF_6) (solid line) and **3b** (dashes) in dichloromethane.

In the visible to near-infrared region, the broad composite bands are characteristic of oxo-centered Ru_3O clusters with delocalized electronic structures.[17,21] These low energy bands, arising from intracluster (IC) transitions, are highly dependent on the electron content or formal oxidation state of the Ru_3O clusters.[16,17,24] Compared with the low energy band (704 nm) of [**2**]$^+$ containing a $[Ru_3^{III,III,III}]^+$ moiety, that of the neutral compound **2a** (778 nm) containing a $[Ru_3^{III,III,II}]^0$ moiety shifts significantly to a lower energy. As shown in Fig. 3, the IC band energy is obviously red-shifted from [**3**]$^{2+}$ (727 nm) to [**3a**]$^+$ (752 nm) and from [**3a**]$^+$ (752 nm) to **3b** (814 nm), respectively. The decrease in energy for these transitions by stepwise one-electron reduction reflects a gradual rise of the occupied dπ levels as the electron number increases.[17,24] As depicted in Fig. 3, it is noteworthy that the IC absorption envelope of the 1+ complex [**3a**]$^+$ (752 nm) containing one $[Ru_3^{III,III,III}]^+$ moiety and one $[Ru_3^{III,III,II}]^0$ moiety is between the 2+ complex [**3**]$^{2+}$ (727 nm) containing two $[Ru_3^{III,III,III}]^+$ moieties and the neutral complex **3b** (814 nm) containing two $[Ru_3^{III,III,II}]^0$ moieties. The intervalence charge transfer (IVCT) band in the 1+ dimeric complex [**3a**]$^+$ with intercluster mixed-valency, nevertheless, is unobserved in the scanning range 200–3000 nm due probably to the low extinction coefficient of this band, which is likely covered by intense intracluster electronic transitions.

The electronic absorption bands of the $[Ru_3O]^{n+}$ (n = 0 or 1) clusters are obviously affected by dimerization. Compared with those in [**2**]$^+$ (330 and 704 nm), the CLCT (350 nm) and IC (727 nm) bands in the dimeric complex [**3**]$^{2+}$ shift to a lower energy. The same phenomenon is also found between the neutral complex **2a** and its dimer **3b**. The distinct red shifts in absorption energy from the $[Ru_3O]^{n+}$ (n = 0 or 1) complexes to their corresponding dimeric species $[\{Ru_3O\}(\mu_4\text{-bpym})\{Ru_3O\}]^{n+}$ (n = 0 or 2) arise probably from the strong intercluster interaction across *ortho*-metallated bpym.[23–25]

In summary, a feasible synthetic route is established to prepare delocalized Ru_3O cluster derivatives with *ortho*-metallated bpym. Structural characterization demonstrates unambiguously that bpym exhibits an unprecedented μ_4-η^1(C),η^1(C),η^2(N,N), η^2(N,N) bonding mode. A significant cluster–cluster interaction between Ru_3O cluster moieties is mediated across bridging *ortho*-metallated bpym.

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Notes and references

‡ Crystal data for [**3a**](PF_6)·Et_2O·H_2O: $C_{52}H_{66}F_6N_8O_{24}PRu_6$, M_r = 1938.52, monoclinic, space group $C2/c$, a = 29.7237(1) Å, b = 15.6233(2) Å, c = 16.6929(1) Å, β = 98.41(1)°, V = 7668.49(11) Å^3, Z = 4, ρ_{calc} = 1.679 g cm^{-1}, μ(Mo-K$_\alpha$) = 1.259 mm^{-1}, T = 293(2) K, R_{int} = 0.0459, 5005 unique reflections, $R1$ = 0.0692, w$R2$ = 0.1538 for 4330 reflections with $I > 2\sigma(I)$, $R1$ = 0.0853, w$R2$ = 0.1622 for all data, GOF = 1.292. CCDC 281053. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601611a

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