Synthesis and Properties of the Geometrically Controlled Mixed-Valence Tetrahedral $Ru^{II}_2Ru^{III}_2L_6$ Cluster

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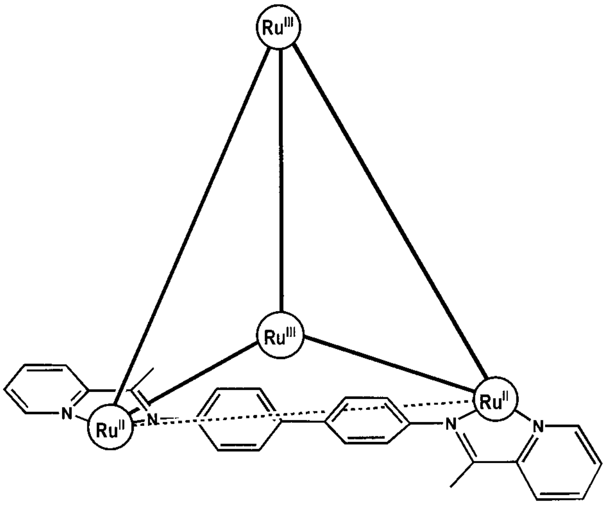
The reaction of $Ru(DMSO)_4Cl_2$ and *N,N′*-bis[1-(pyridin-2-yl)-ethylidene]benzidine (L) in the presence of $NaClO_4$ afforded the tetranuclear ruthenium compound, $Ru_4L_6·10ClO_4$, by self-assembly. Magnetic and electrochemical measurements clearly indicated the presence of both Ru^{II} and Ru^{III} moieties within the tetrahedral ruthenium cluster. The Robin-Day Class II mixed-valence behavior was supported by the UV/Vis-NIR spectra with the electronic coupling parameter V_{ab} of 200 cm^{-1}. It is demonstrated that the mixed-valence $Ru^{II}_2Ru^{III}_2L_6$ cation was stabilized by controlling the coordination geometries of the ruthenium ions between octahedral and trigonal prismatic to fit the supramolecular structure of the tetranuclear cluster.

Introduction

It is well established that the self-assembly processes may generate, in a spontaneous and direct manner,[1] well-defined architectures that are dependent on numerous factors such as the nature of the coordination sites, the structures of the bridging ligands, the geometric preferences of the metal ions, and the weak noncovalent interactions. The application of metal–ligand interactions has proved particularly fruitful, and a considerable variety of frequently predesigned molecular architectures have been assembled.[2] Among them, polygonal and polyhedral compounds formed by self-assembly of transition metals have many special functional properties such as luminescence, redox activity and magnetism in addition to their particular structural features.[3] As the simplest platonic polyhedrons, tetrahedral clusters formed by self-assembly of the transition metals have attracted more attention because of their intrinsic beauty and interesting host–guest chemistry, as well as the fact that they illustrate some basic construction principles necessary to assemble high-symmetry clusters.[4]

On the other hand, mixed-valence species have played a dominant role as simple model systems in the investigation of electron-transfer (ET) processes.[5] With respect to the artificial ET model systems consisting of two redox centers separated by saturated or unsaturated spacers, enormous effort and ingenuity have gone into studying the details of the factors influencing the metal–metal interaction, and a great deal of progress has been made.[6] However, relatively little is known about the process of electron transfer between a single donor and acceptor as influenced by their inclusion into larger supramolecular assemblies.[7] In an effort to study electron delocalization in more symmetric polynuclear systems, we have adopted a synthetic approach to assembling high-nuclear mixed-valent metallomacrocycles.[8]

In this contribution, we report a new tetrahedral Ru_4L_6 complex assembled from the rigid imine-based ligand L, *N,N′*-bis[1-(pyridin-2-yl)ethylidene]benzidine, (Scheme 1) with two binding sites separated by a biphenyl group.[9] It is expected that the rigidity of the designed ligand imposes a special geometry on the metal centers by fitting them into the tetrahedral geometry of the cluster (Scheme 1) and that



Scheme 1. The tetrahedral structure of complex **1** including a perchlorate anion within its cavity.

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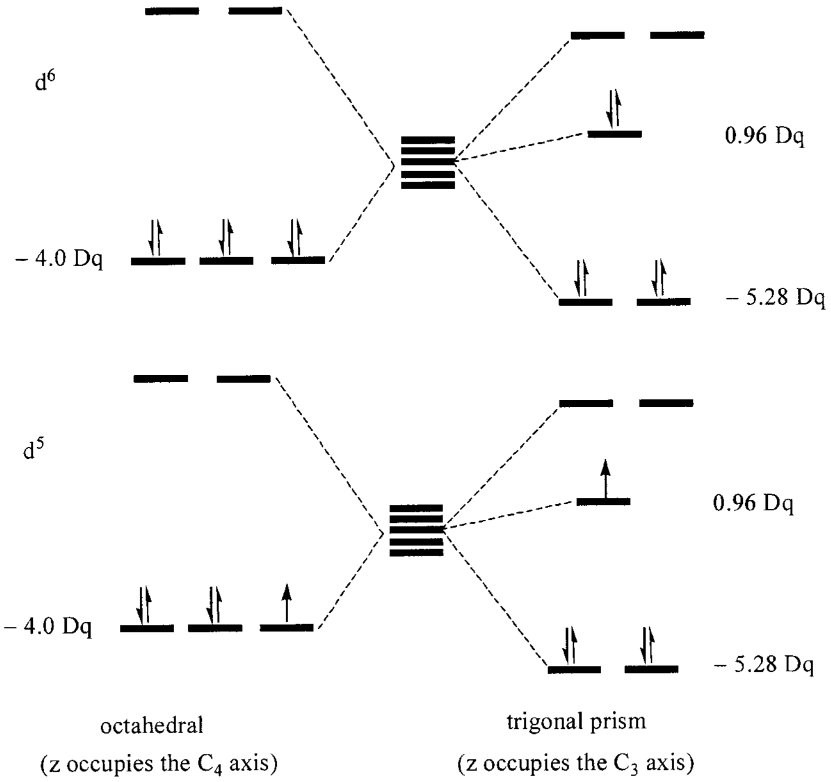

Scheme 2. The energy level of the *d* orbitals in the octahedral and trigonal prismatic coordination fields.

the resulting conformational restriction allows the modification of the redox potentials to form the mixed-valence species, similar to some metal proteins as well as many synthetic analogs.[8,10] In fact, tetranuclear copper and zinc cations $Cu_4L_6^{8+}$ and $Zn_4L_6^{8+}$ have been reported, in which the geometry at the metal center is between octahedral and trigonal prismatic,[9] but mixed-valence behavior was not exhibited, owing to the lack of suitable electronic structures. On the basis of the electronic structures of the d^5 and d^6 metal centers in the octahedral and trigonal prismatic coordination fields (Scheme 2),[11] it should be suggested that the Ru^{II} and Ru^{III} ions coexist in the clusters, because the Ru^{III} ion is more stable than the Ru^{II} ion in the trigonal prismatic coordination field, whereas the Ru^{II} ion has higher stability relative to the Ru^{III} ion in the octahedral coordination field.

Results and Discussion

Treatment of $Ru(DMSO)_4Cl_2$ with the imine-based ligand L in the presence of $NaClO_4$ afforded the tetranuclear ruthenium compound **1** in 44% yield by self-assembly. Elemental analysis and spectroscopic studies suggested the formula $Ru_4L_6 \cdot 10ClO_4$ for compound **1**. The ESI-MS spectrum exhibited an intense peak at *m/z* 316.4 corresponding to $[Ru_4L_6 \subset ClO_4]^{9+}$, which was consistent with the formation of the tetrahedral species. The perchlorate anion was included within the cavity of the cluster like that of the copper and zinc analogs.[9] The tetrahedral ruthenium cation was the major species in the solution, even under the conditions of electrospraying. To determine the coexistence of Ru^{II} and Ru^{III} ions as well as their molar ratio, the temperature-dependent magnetic behavior of compound **1** was investigated (Figure 1). The effective magnetic moment (μ_{eff}) at room temperature of 2.58 μ_B was consistent with the

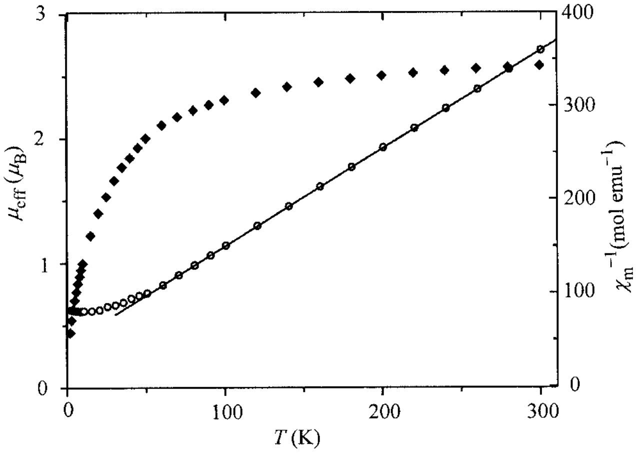

Figure 1. The temperature dependence of the molar magnetic susceptibility μ_{eff} and the reciprocal of the effective magnetic moment χ_m^{-1} for **1**. Open points represent the observed results, and the solid line represents the fitting curve based on the Curie–Weiss law.

value expected for two independent Ru^{III} ions. The value of μ_{eff} decreased slightly with decreasing temperature (2.17 μ_B at 70 K). Below 70 K, the μ_{eff} decreased rapidly and reached 0.44 μ_B at 2 K. It seemed that the two Ru^{III} ions exhibited antiferromagnetic coupling, which was further suggested by a negative Weiss constant [θ = –35.5(2) K] using the data for temperatures greater than 70 K.

In the cyclic voltammograms (CV) of complex **1**, two metal-based reduction waves were observed in the region between 0.4 and 0.7 V and one metal-based broad wave at about 0.9 V. In order to obtain more accurate values of the reduction/oxidation peaks, the differential pulse voltammetry (DPV) technique was employed.[12] DPV measurements (Figure 2) of complex **1** exhibited three main peaks at 0.46, 0.60, and 0.89 V (vs. SCE). Considering the results of the CV experiments, it was helpful to confirm by DPV that the peaks at 0.6 and 0.46 V were reduction peaks, whereas the peak at 0.89 V corresponded to oxidation. Not surprisingly, the first redox potential is much smaller than that of the [Ru(bpy)$_3$]$^{2+}$ moiety and most of the mononuclear and polynuclear bpy–Ru complexes,[13] since the ruthenium centers in complex **1** are coordinated in a geometry between octahedral and trigonal prismatic, like those of the tetranuclear zinc and copper M$_4$L$_6$ complexes.[9] It seems that the peaks at 0.46 and 0.60 V of complex **1** were assigned to the single-electron reduction processes [Ru$^{II}{}_3$Ru^{III}]/[Ru$^{II}{}_4$] and [Ru$^{II}{}_2$Ru$^{III}{}_2$]/[Ru$^{II}{}_3$Ru^{III}], respectively. The broad peak at 0.89 V was due to the two overlapping single-electron oxidation processes [Ru^{II}Ru$^{III}{}_3$]/[Ru$^{II}{}_2$Ru$^{III}{}_2$] and [Ru$^{III}{}_4$]/[Ru^{II}Ru$^{III}{}_3$] (Gaussian deconvolution of such a band gives two peaks at 0.79 V and 0.91 V, respectively). It is postulated that such a conformation makes the Ru^{III} moiety exhibit higher stability relative to the common octahedrally coordinated geometry.

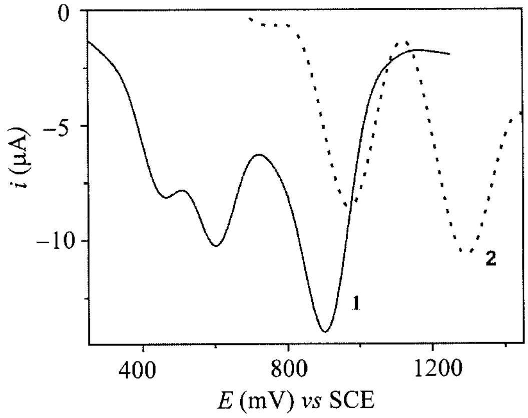

Figure 2. DPV of complexes **1** and **2** in CH$_3$CN solution (0.1 M NBu$_4$ClO$_4$; scan rate 20 mV/s).

To test such a hypothesis, the dinuclear ruthenium complex [Ru$_2$(bpy)$_4$L](ClO$_4$)$_4$ **2**, in which the ruthenium atom is octahedrally coordinated, was synthesized and characterized. DPV measurements for **2** exhibited two oxidation peaks at 0.93 and 1.30 V (vs. SCE) (Figure 2). The first oxidation potential of complex **2** was too high for the Ru^{III} species to be stable in the usual conditions. The ESI-MS spectrum of **2** exhibited one strong peak at m/z 304.5 corresponding to [Ru$_2$(bpy)$_4$L]$^{4+}$, which confirmed that there was no Ru^{III} ion in complex **2**. Clearly, the difference in the coordinative conformation of the metal centers in the two complexes was the important factor on controlling the redox potentials of the Ru^{III}/Ru^{II} couples.

The UV/Vis spectrum of complex **1** exhibits metal-to-ligand charge-transfer (MLCT) for Ru^{II} at 570 nm with a shoulder at about 520 nm, which is red-shifted relative to the same peak for complex **2** (460 nm) (Figure 3). Such results agree well with the related electrochemistry studies, which indicate that the coordination geometries of the ruthenium atoms in the two complexes are significantly different. In the near-IR region, complex **2** does not exhibit any obvious absorption band. However, complex **1** exhibits a LMCT absorption band corresponding to the Ru^{III} moiety at about 11000 cm^{-1} (ε = 5500 cm^2/mol) and a MMCT band at about 7500 cm^{-1} (ε = 2000 cm^2·mol^{-1}) with half-width of 4000 cm^{-1}, respectively. Intervalence charge-transfer bands in mixed-valence Ru^{III}/Ru^{II} complexes generally occurred in the near-IR region of the electronic spectra and had extinction coefficients of several hundred or a few thousand mol/dm^3·cm,[5,6] so both the position and the intensity of the 7500 cm^{-1} peak are consistent with an IT band. Assuming that the MV compound behaves as a Robin-Day Class II compound,[14] the IT absorption band of MV compounds can be modeled by classical Marcus-Hush theory[15] to obtain the electronic coupling parameter.[16] However, there are two Ru^{II} and two Ru^{III} in the complete tetrahedron. This means that the effective concentration in ion pairs Ru^{II}-Ru^{III} is actually four times the actual concentration (ε = 500 cm^2/mol). Considering that the Hush formula is valid for a simple binuclear system, i.e. a single Ru^{II}–Ru^{III} pair, the electronic coupling parameter of compound **1** can be given as 200 cm^{-1}. Significantly, the coordination environment of the metal centers in geometrically

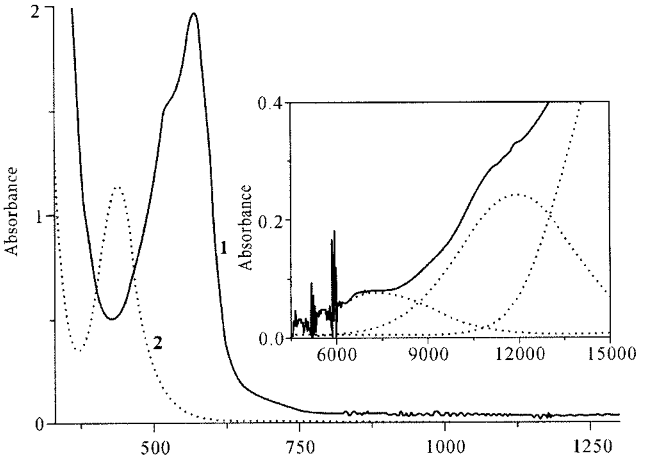

Figure 3. The UV/Vis-NIR spectra of the complexes **1** and **2** in acetonitrile (2.0 ×10^{-5} M). The insert showed the near-IR spectrum of the complex **1** in acetonitrile (5.0×10^{-5} M). The Gaussian fits (the dot lines) showed the LMCT band at 11000 cm^{-1} and the MMCT band at 7500 cm^{-1}, respectively.

constrained tetrahedral architectures plays an important role in controlling the redox potential of the Ru^{III}/Ru^{II} couples and modifying metal–metal interactions.

In summary, this paper describes a modular approach to a mixed-valence compound implemented by controlling the coordination geometry of ruthenium ions to fit the architecture in the tetranuclear cluster. Mixed-valence compounds have played a crucial role not only in the exploration of electron-transfer theory but also for addressing contemporary issues in electron-transfer research, especially when the emphasis in this field has shifted away from simple dinuclear MV species and focused on multinuclear supramolecular species.[17,18]

Experimental Section

General: All chemicals were of reagent grade quality; they were obtained from commercial sources and used without further purification. $Ru(DMSO)_4Cl_2$,[19] the ligand[9] and *cis*-$Ru(bipy)_2Cl_2 \cdot 2H_2O$[20] were synthesized according the literature methods. The elemental analyses of C, H, and N were performed with a Perkin–Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. Electrospray mass spectra were recorded with a LCQ system (Finnigan MAT, USA) using methanol as the mobile phase. IR spectra were recorded with a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Variable-temperature magnetic susceptibility data were obtained on polycrystalline samples at 2–300 K in a magnetic field of 10 Koe after zero-field cooling using a MagLab System 2000 magnetometer. Diamagnetic corrections were estimated from Pascal's constants. Differential pulse voltammetry (DPV) was done with an EG and GPAR model 273 instrument in a three-electrode cell with a pure Ar gas inlet and outlet. The working electrode and counter electrode were Pt spirals, and the reference electrode was a saturated calomel electrode (SCE). DPV experiments were performed with a scan rate of 20 mV/s. Uv/Vis-NIR spectra were obtained in acetonitrile solution at room temperature with a Shimadzu 3100 spectrophotometer.

Preparation of Complex 1: The ethanol solution of the mixture $Ru(DMSO)_4Cl_2$ (0.58 g, 1.2 mmol) and the ligand L (0.71 g, 1.8 mmol) was refluxed for 12 h. Dark blue precipitate $(Ru_4L_6)(ClO_4)_{10}$ was formed when the solution was added to a saturated ethanol solution of $NaClO_4$. Purification was performed by chromatography on a neutral alumina column (20 × 1.5 cm) with CH_3CN/MeOH, 1:1 (v/v) as eluent. The dark-blue fraction was collected and concentrated to a small volume. Upon addition of ethanol, complex **1** was obtained as a dark solid. Yield 0.48 g (44%). $Ru_4C_{156}H_{132}Cl_{10}N_{24}O_{40}$ (3738.2): calcd. C 50.1, H 3.6, N 9.0; found C 49.8, H 4.1, N 8.7. UV/Vis (logε) in methanol: 287 (4.8), 448 (4.3), 481 (4.6) nm. IR: 3444 ($\nu_{C–H}$), 1634, 1539, 1504, 1463 ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{C–N}$), 1092, ($\nu_{Cl–O}$), 837, 770, 736 ($\delta_{C–H}$) cm^{-1}.

Preparation of Complex 2: $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ (0.15 g, 0.31 mmol) and L (0.06 g, 0.15 mmol) were refluxed in ethanol (50 mL) for 12 h under nitrogen. When this solution was added to a saturated ethanol solution of $NaClO_4$, $[Ru_2(bipy)_4L](ClO_4)_4$ separated out as a red precipitate, which was collected by filtration, washed with water and ethanol for several times, and dried in vacuo over P_4O_{10}. Yield: 0.15 g (68%). $C_{66}N_{12}H_{54}Ru_2Cl_4O_{16}$ (1614.1): calcd. C 49.1, H 3.4, N 10.4; found C 49.2, H 3.2, N 10.3. ^1H NMR ($[D_6]$DMSO): δ = 8.87 (t, 2 H, Py), 8.67 (d, 2 H, Py), 8.62 (d, 2 H, Py), 8.50 (t, 4 H, bipy), 8.22 (m, 8 H, bipy), 8.01 (d, 4 H, Ph), 7.96 (m, 4 H, bipy), 7.86 (d, 2 H, Py), 7.72 (d, 4 H, bipy), 7.68 (d, 4 H, Ph), 7.35 (t, 2 H, bipy), 6.90 (d, 2 H, bipy), 6.84 (d, 4 H, bipy), 6.69 (d, 4 H, bipy), 1.62 (s, 6 H, CH_3) ppm. UV/Vis (log ε) in CH_3CN: 289 (4.2), 347 (3.2), 466 (3.4) nm. IR: 3426 ($\nu_{C–H}$), 1464, 1445, 1422 ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{C–N}$), 858, 766, 624 ($\delta_{C–H}$), 1092, ($\nu_{Cl–O}$) cm^{-1}.

Caution! Although no problems were encountered in this work, perchlorates are potentially explosive and should be handled with care.

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