A paramagnetic quasi-1D chain comprised of Pt/Rh possessing an unpaired electron

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Abstract

In this manuscript we review the structure of the novel 1-D chain complex, \([\text{PtRh}(\text{PVM})_2(\text{NH}_3)_2\text{Cl}_2.5]_2[\text{Pt}_2(\text{PVM})_2(\text{NH}_3)_4]_2(\text{PF}_6)_6\) \(_2\text{MeOH}\) \(_2\text{H}_2\text{O}\) \(_n\) (PVM = pivalamidate), consisting of mixed-valence dimeric complexes with appreciably extended metal–metal bondings. Compound 4 is made up of octameric segments, each of which consists of two platinum-rhodium dinuclear complexes and a tetrameric platinum unit. The charge of 19+ for the Pt6Rh2 octameric segment in 4 was deduced from the number of the independent PF6⁻ counter ions, and is the supporting evidence for one unpaired electron per one octameric segment. The tetrameric platinum unit in 4 is the structural motif that is observed in \([\text{Pt}_2(\text{PVM})_2(\text{NH}_3)_4](\text{PF}_6)_2\) \(_2\text{H}_2\text{O}\) \(_2\) and \([\text{Pt}_4(\text{PVM})_4(\text{NH}_3)_8](\text{PF}_6)_4(\text{ClO}_4)_2\) \(_2\text{H}_2\text{O}\) (3 = “platinum blue” with one electron delocalized over the four platinum atoms). On the basis of the EPR, magnetic susceptibility, and electrical conductivity results, the nature of the unpaired electron in 4 is discussed.

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Keywords: Platinum Blue; 1-D Chain; Mixed-valence; Rhodium

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1. Introduction

One-dimensional (1-D) materials have long fascinated physicists and chemists because of their unusual physical properties [1]. It has been recognized that stacks of mixed-valent organic and inorganic molecules exhibit unusual electrical properties due to the alternate donor–acceptor interactions within the stack column [2]. One of the future goals of this area is to prepare “synthetic metals”, and to establish the superconducting state in low-dimensional materials [3,4]. For the rationally synthesis of electron-conducting 1-D materials, a judicious choice of mixed-valence metal complexes (Pt, Rh, etc.) is necessary [5–15].

Previously, we reported the synthesis and crystal structure of [Pt(PVM)2(NH3)4](PF6)2 [16,17]. Complex I can easily bind a second metal ion (platinum/hetero-metals) with the non-coordinated oxygen atoms in the amidate moieties, affording various dinuclear Pt complexes [16,17]. Furthermore, we succeeded in obtaining a novel 1-D chain from the reaction of Pt–Pt and Pt–Rh dinuclear complexes (Scheme 1) [18]. We review here the structures and unique magnetic properties of the 1-D chain complex.

2. Experiment

Pivalonitrile and sodium hexafluorophosphate were obtained from Tokyo Kasei Industrial Co. Rhodium(III) chloride trihydrate was obtained from Kanto Chemical Co. K2PtCl4 was obtained from Tanaka Kikinzoku Co. [Pt(PVM)2(NH3)2]·2H2O (1, PVM = pivalamidate) was prepared according to the previously reported procedure [16]. [Pt4(PVM)4(NH3)8](PF6)4(ClO4)2·6H2O (2) was obtained by slow evaporation of the MeOH solution containing 1 and excess NaPF6. [Pt4(PVM)4(NH3)8](PF6)4(ClO4)2·2H2O (3) was synthesized by mixing 1, [Pt(PVM)2(OH)2](ClO4)2·6H2O, and NaPF6 in water. ([PtRh(PVM)2(NH3)2Cl2.5](PF6)2·2MeOH·2H2O)n (4) was obtained by slow evaporation of the MeOH solution containing 1, RhCl3·3H2O, and excess NaPF6. The details of the synthetic methods were described in the previous report [18].

3. Results and discussion

3.1. Crystal structures

3.1.1. [Pt2(PVM)2(NH3)4](PF6)2·7H2O (2)

Fig. 1a shows the crystal structure of 2. Each platinum atom in the dinuclear complex is cis coordinated with two ammine ligands and either of two oxygen atoms or two deprotonated nitrogen atoms from two PVM ligands. The two dinuclear complexes constituting the tetrameric chain are related through a crystallographically inversion center. Within the dinuclear complex, the Pt(1)–Pt(2) bond distance is 2.9546(11) Å. The platinum coordination planes are tilted by 27.3° with respect to one another and, in addition, are twisted by 1.3° about the platinum–platinum bond axis. It is known that the tetraplatinum chain structures are achieved only with the head-to-head (HH) dinuclear complexes, where the dimer–dimer interactions are generally stabilized by a Pt–Pt bond and/or four hydrogen bonds formed between the oxygen atoms of amidate and the hydrogen atoms of the ammine ligands. This tetracnuclear structure is basically identical with those of the previously reportedones with other amidate ligands [19–22]. The X-ray analysis revealed that four PF6 ions exist per one tetrancnuclear unit, and therefore the platinum oxidation states of 2 are +2.

3.1.2. [Pt4(PVM)4(NH3)8](PF6)4(ClO4)2 ·2H2O (3)

Fig. 1b shows the crystal structure of 3. The single crystal of 3 also consists of a tetranuclear chain of platinum atoms linked through amidate bridges and hydrogen bonds. Within a dinuclear complex, the Pt(1)–Pt(2) bond distance is 2.8039(9) Å. The platinum coordination planes are tilted by 21.8° with respect to one another and, in addition, are twisted by 0.7° about the platinum–platinum bond axis. An important difference between 2 and 3 is the average platinum oxidation states; the existence of four PF6 and one ClO4 ions per tetranuclear unit in 3 indicates that platinum oxidation states of 3 are +2.25. Thus, complex 3 is recognized as “platinum blue” [23–27], which has a linear tetracnuclear metal–metal bonded backbone.

Scheme 1. The reaction scheme of [Pt(PVM)2(NH3)2]·2H2O (1) which can easily bind a second metal ion affording various dinuclear Pt complexes. The ligand-unsupported Pt(II)–Rh(II) bond is formed by the simple reaction of the Pt–Pt dinuclear complex with the Pt–Rh dinuclear complex.
Fig. 1. ORTEP drawing of: (a) \([\text{Pt}_2(\text{PVM})_4(\text{NH}_3)_4](\text{PF}_6)_2 \cdot \text{H}_2\text{O} \ (2)\), (b) \([\text{Pt}_2(\text{PVM})_4(\text{NH}_3)_4](\text{PF}_6)_4(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O} \ (3)\), and (c) \([\text{PtRh}(\text{PVM})_2(\text{NH}_3)_2\text{Cl}_{2.5}]_2[\text{Pt}_2(\text{PVM})_2(\text{NH}_3)_4](\text{PF}_6)_6 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}]_n \ (4)\). The hydrogen atoms, \(\text{PF}_6\) ions, and solvent molecules (\text{MeOH} and \text{H}_2\text{O}) are omitted for clarity.

Fig. 2. (a) Crystal structures of \([\text{PtRh}(\text{PVM})_2(\text{NH}_3)_2\text{Cl}_{2.5}]_2[\text{Pt}_2(\text{PVM})_2(\text{NH}_3)_4](\text{PF}_6)_6 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}]_n \ (4)\) with a schematic drawing of the metal-metal bond lengths. The hydrogen atoms, \(\text{PF}_6\) ions, and solvent molecules (\text{MeOH} and \text{H}_2\text{O}) are omitted for clarity. (b), (c) Crystal packing diagram of the 1-D chains in 4.
with Pt(+2.25)4 mixed-valence, and the one unpaired electron is delocalized over the four platinum cores.

3.1.3. \{[PtRh(PVM)2(NH3)2Cl2.5J2J[Pt2(PVM)2(NH3)4](PF6)6]/C12MeOH/C12H2O\}n (4)

Fig. 1c form the crystal structure of 4. The most remarkable structural feature is that the complex cation is an infinite repetition of the octameric segment of Pt6Rh2 bridged by Cl− ion, with a crystallographic inversion center at the center of the octamer (Fig. 2a). The Pt6Rh2 octameric segment consists of four dimeric units (inner dinuclear complexes; Pt(1)–Pt(2), Pt(1′)–Pt(2′), outer dinuclear complexes; Rh(1)–Pt(3), Rh(1′)–Pt(3′)), each doubly bridged with PVM ligands. The inner tetrameric platinum unit (Pt(2)–Pt(1)–Pt(1′)–Pt(2′)) has the structure quite similar to 2 and 3. The central inter-dimer interaction is reinforced by four hydrogen bonds between the oxygen atoms of PVM and the hydrogen atoms of the ammine ligands. The distance between the PVM-bridged platinum atoms (Pt(1) and Pt(2)) of 2.8540(7) Å is 0.218 Å shorter than the inner Pt(1)–Pt(1′) distance of 3.0634(10) Å. The outer dimers, [PtRh(PVM)2(NH3)2Cl2]n+(Pt(3)–Rh(1) = 2.5987(11) Å), are bonded to both ends of the tetranuclear platinum unit with the distance of Pt(2)–Rh(1) = 2.7337(11) Å and the typical torsion angle of 45°.

In addition, the Pt6Rh2 octameric segments are bridged by Cl− ligands (Pt(3)–Cl(3) = 2.5959(6) Å) to give a very attractive pseudo-1-D infinite chain with the expression of \[−Pt−Rh−Pt4−Rh−Pt−Cl−n\]. Each infinite chain extends in parallel to the neighboring ones as shown in Fig. 2b and 2c. The charge of 19+ for the Pt6Rh2 octameric segment in 4 was determined from the number of the independent PF6− ions, which is exactly six in the X-ray refinement of the ion occupancies. These results provide convincing evidence for the description of the material to be composed of Pt and Rh atoms with one unpaired electron per Pt6Rh2Cl unit.

3.1.4. Comparison of bond distances and angles between 2, 3, and 4

Table 1 summarizes the selected bond distances and angles of the tetrameric platinum units in 2–4. Both of the inter-dimer and intra-dimer Pt–Pt distances in 4 are slightly longer than the corresponding lengths of 3, but still much shorter than the corresponding lengths in 2. The lengths of the hydrogen bonds between the amide oxygen and ammine nitrogen atoms in the inter-dimers observed in 4 is also between those of 2 and 3. The tilt angle (τ) between the Pt(1) and Pt(2) coordination planes increases as the Pt–Pt distance increases, as observed in the comparison of the x-pyrollidonate-tan [28], -blue[27] and -yellow [22]. The relation that the Pt–Pt distance increases with decreasing average platinum oxidation state is widely observed in this class of compounds [28]. Assuming this relation holds in 4, the average oxidation state of the inner tetrameric platinum unit in 4 appears to be between 2.0+ and 2.25+.

3.2. Physical measurements

The quasi-1D system 4, which is distinct from the previous systems on the ground that two kinds of metals

![Fig. 3. The CW EPR spectra of: (a) 3 in water/ethyleneglycol (= 1:1 v/v) glass (at 77 K), and powder samples of (b) 3 (at 77 K), (c) 4 (at 77 K), and (d) 4 (at r.t.). Asterisks exhibit the impurity corresponding to the platinum blue (around 270 mT). The solid lines are the measured spectra and the dotted lines are the simulations.](image-url)
are conjugated in the system, exhibits the unique metal-metal interaction and magnetic properties.

3.2.1. EPR measurements

Fig. 3 shows the EPR spectra of 3 in water/ethyleneglycol (1:1 v/v) glass and powder samples of 3 and 4. The EPR spectrum of 3 in the glass exhibits sharp perpendicular and parallel peaks, each with split into at least nine lines due to $^{195}$Pt nuclei ($I = 1/2$ with the abundance of 33.7%). The EPR parameters have been determined by computer simulation as $g_\perp = 2.393$, $g_\parallel = 1.979$, $A_\perp = 429$ MHz, $A_\parallel = 499$ MHz, $A_{\perp\parallel} = 861$ MHz, $A_{\parallel\perp} = 679$ MHz. These values are characteristic of platinum blue, being similar to the literature values [24,29,30].

Powdered 3 shows a broad axial-type signal with no resolved hyperfine splittings ($g_\perp = 2.350$, $g_\parallel = 2.030$; peak-to-peak line width, $W_\perp = 12.5$ mT, $W_\parallel = 12.5$ mT), whereas the powder sample of 4 exhibits a much broader signal centered at a smaller $g_{av}$ value; $g_{av} = 2.032$, $W = 45.0$ mT (at 77 K), $g_{av} = 2.034$, $W = 44.0$ mT (r.t.).

3.2.2. Comparison of $g$ values between 3, 4, and reported compounds

The obtained $g$ values for 3 are well interpreted in terms of a $d_{z^2}$-hole state ($z$ along the mean Pt chain) with an admixture of the lower lying $d_{xz}$, $d_{yz}$ states due to the spin–orbit coupling [29,30]. Typical examples for $d_{z^2}$-type Pt complexes, Pt(IV)-doped [Pt(NH$_3$)$_4$][PtCl$_4$]$_2$-pyridone blue [24], and K$_2$Pt(CN)$_3$Br$_{1/3}$·3H$_2$O [32], are summarized in Table 2. All these values are attributed to the $d_{z^2}$-hole state of Pt(III).

The EPR spectrum of 4 is quite different from that of 3, and is featured by (i) the relatively small $g_{av}$ value and (ii) the broad-spectrum profile. Taking into account that the $g_{av}$ value of 4 ($g_{av} = 2.032$) is much smaller than those of the $d_{z^2}$-type Pt complexes, it is unlikely that the unpaired electron occupies the $d_{z^2}$ state in 4. It is important to note that the $d_{z^2}$-type Rh(II) complexes possess relatively large $g_{av}$ value similar to Pt(III) (e.g., $g_{av} = 2.176$ for (TTiPP)Rh(II) (TTiPP = tetrakis(1,3,5-triisopropylphenyl)porphyrin)) [33]. Considering the small $g_{av}$ value of 4 which is different from both Pt(III) and Rh(II), the singly occupied orbital in 4 is attributed most likely to the Rh(II) $d_{xy}$ orbital, which is raised above $d_{z^2}$ by the $\pi$ interaction with the amidate ligands (Scheme 2). The broad nature of the EPR spectrum of 4 can be attributed to a long-distance exchange interaction.
3.2.3. Magnetic properties of 3 and 4

Magnetic susceptibility measurements for 3 and 4 were carried out in the temperature range of 2–250 K, and results were shown in Fig. 4. Similar to previous reports [24], the value of 1.27 \( \mu_{\text{eff}} \) for the effective magnetic moment in 3 indicates the presence of one unpaired electron per \([\text{Pt}_4(\text{PVM})_4(\text{NH}_3)_8]^{5+}\) cation. Since the tetranuclear platinum units pack in a random fashion, there are no long-range exchange interactions in 3. On the other hands, the \( \mu_{\text{eff}} \) of 4 is reduced with the decrease of the temperature. The plot of \( 1/\chi_m \) vs. \( T \) follows the Curie–Weiss law with the Weiss constant \( \theta = -31.9 \text{ K} \), indicating an antiferromagnetic interaction between the paramagnetic \( \text{Pt}_6\text{Rh}_2 \) segments.

3.2.4. Electrical conductivity of 4

Fig. 5 shows the single-crystal electrical conductivity of 4 (4 probes, DC). The X-ray characterization revealed that the planes 1 0 1 and 0 1 0 are parallel to the ridgelines in the rhombic crystal of 4. Because of the thin plate crystal, it was impossible to measure the electrical conductivity parallel to the chain, and only the conductivity perpendicular to the chain direction was measured. The electrical conductivity of 4 exhibited a semiconducting character of the material \( (3.52 \times 10^{-8} \text{ S cm}^{-1}) \) at room temperature. Compound 4 shows a typical semiconducting behavior in the temperature range measured \( (267–295 \text{ K}) \). The inset is the plots of logarithms of the electrical conductivity versus reciprocal of absolute temperature, yielding a straight line whose gradient gives \( \Delta E = 1.0 \text{ eV} \) as the activation energy.

4. Conclusion

This manuscript reviews that the linear chain structure of the amidate-bridged platinum tetramer can be extended to the octameric segment \( \text{Pt}_6\text{Rh}_2 \), which is further extended to infinity by \( \text{Cl}^- \) bridges. The Pt–Rh bond between the Pt–Rh dinuclear complex and the Pt tetramer is the first example of metal–metal bond formed between the tetranuclear platinum chain and any other metal, and suggests that, by selecting suitable metal ions, the tetranuclear platinum chain can be incorporated into a longer chain by metal–metal bonds. It is also noteworthy that the unpaired electron in complex 4 is not on the \( d_{z^2} \) orbital of the tetranuclear platinum chain, but is on the \( d_{xy} \) of the rhodium atom and hops from one rhodium atom to another. This kind of long-distance exchange is rare and possibly leads to new electric and magnetic properties.

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