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Review

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, $\{[PtRh(PVM)_2(NH_3)_2Cl_{2.5}]_2[Pt_2(PVM)_2(NH_3)_4]_2(PF_6)_6 \cdot 2MeOH \cdot 2H_2O\}_n$ (**4**) (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 Pt_6Rh_2 octameric segment in **4** was deduced from the number of the independent PF_6^- 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 $[Pt_2(PVM)_2(NH_3)_4](PF_6)_2 \cdot H_2O$ (**2**) and $[Pt_4(PVM)_4(NH_3)_8](PF_6)_4(ClO_4) \cdot 2H_2O$ (**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.

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

Contents

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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 $[Pt(PVM)_2(NH_3)_2] \cdot 2H_2O$ (**1**, PVM = pivalamidate) [16,17]. Complex **1** can easily bind a second metal ion (platinum/hetero-metals) with the non-coordinated oxygen atoms in the amidate moieties, affording various dinuclear and trinuclear 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. K_2PtCl_4 was obtained from Tanaka Kikinzoku Co. $[Pt(PVM)_2(NH_3)_2] \cdot 2H_2O$ (**1**, PVM = pivalamidate) was prepared according to the previously reported procedure [16]. $[Pt_2(PVM)_2(NH_3)_4](PF_6)_2 \cdot H_2O$ (**2**) was obtained by slow evaporation of the MeOH solution containing **1** and excess $NaPF_6$. $[Pt_4(PVM)_4(NH_3)_8](PF_6)_4(ClO_4) \cdot 2H_2O$ (**3**) was synthesized by mixing **1**, $[Pt(PVM)_2(OH_2)_2](ClO_4)_2$, and $NaPF_6$ in water. $\{[PtRh(PVM)_2(NH_3)_2Cl_{2.5}]_2[Pt_2(PVM)_2(NH_3)_4]_2(PF_6)_6 \cdot 2MeOH \cdot 2H_2O\}_n$ (**4**) was obtained by slow evaporation of the MeOH solution containing **1**, $RhCl_3 \cdot 3H_2O$, and excess $NaPF_6$. The details of the synthetic methods were described in the previous report [18].

3. Results and discussion

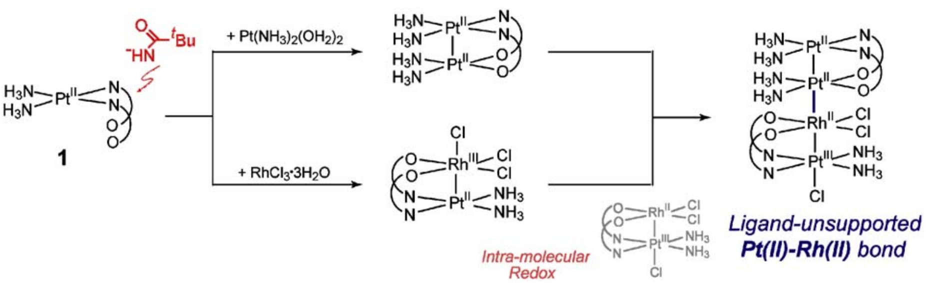
3.1. Crystal structures

3.1.1. $[Pt_2(PVM)_2(NH_3)_4](PF_6)_2 \cdot H_2O$ (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 tetranuclear structure is basically identical with those of the previously reported ones with other amidate ligands [19–22]. The X-ray analysis revealed that four PF_6^- ions exist per one tetranuclear unit, and therefore the platinum oxidation states of **2** are +2.

3.1.2. $[Pt_4(PVM)_4(NH_3)_8](PF_6)_4(ClO_4) \cdot 2H_2O$ (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 PF_6^- and one ClO_4^- 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 tetranuclear metal–metal bonded backbone



Scheme 1. The reaction scheme of $[Pt(PVM)_2(NH_3)_2] \cdot 2H_2O$ (**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.