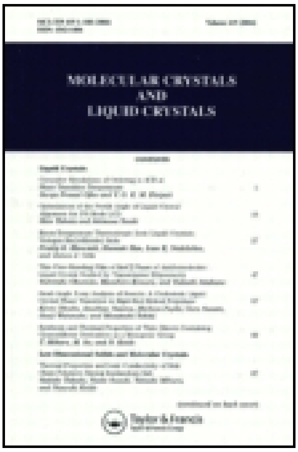

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# Polymer Complexes of Rhodium Acetamidate Dimers Bridged by Pyrazine, 4,4′-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane

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# Polymer Complexes of Rhodium Acetamidate Dimers Bridged by Pyrazine, 4,4′-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane

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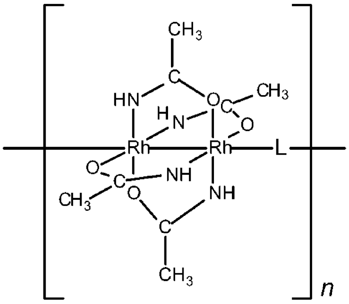
Polymer complexes of rhodium (II,II and II,III) acetamidate dimers bridged by pyrazine (pyz), 4,4’-bipyridine (4,4’-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco) have been prepared and characterized. Doping of the Rh(II,II) polymers with $NOBF_4$ increased the electrical conductivities when the bridging ligands were pyz and 4,4’-bpy. The magnetic interaction through the bridging ligands was found to be weak for the Rh(II,III) polymers.

Keywords: polymer complexes; rhodium acetamidate; pyrazine; 4,4’-bipyridine; 1,4-diazabicyclo[2.2.2]octane; magnetism; conductivity

## INTRODUCTION

Recently, much interest has been devoted to polymeric transition metal complexes bridged by a ligand regarding their unique magnetic and conductive properties[1-3]. We have been making efforts to prepare such polymeric complexes using $[M_2(O_2CR)_4]$ dimers (M = Ru, Rh) and bidentate bridging ligands, pyrazine (pyz), 4,4’-bipyridine (4,4’-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco). In the case of M = Rh(II), we prepared and characterized the polymers $[Rh_2(O_2CCMe_3)_4L]$ (L = pyz, 4,4’-bpy, and dabco)[4], being followed by the study on their chemical oxidation to obtain the polymers including Rh(II,II) and Rh(II,III) dimer units from the expectation that the partially oxidized ones could increase their electrical conductivities as being reported for the other coordination polymers[2,3]. However, the oxidation is unsuccessful so far. This is due to the fact that the dimer is highly resistant to the oxidation (the Rh(II,II)/Rh(II,III) redox potential is 1.12 V in *o*-dichlorobenzene (vs. SCE))[5]. The polymer complexes of ruthenium(II) acetate $[Ru_2(O_2CMe)_4L]_n$ (L = pyz, 4,4'-bpy, and dabco) were also prepared and, in this case, oxidized with ease. The obtained conductivities were $\sigma = 10^{-6} \sim 10^{-7}$ S $cm^{-1}$ when they were partially oxidized[6]. We here present the polymer complexes (Scheme 1) of rhodium(II) acetamidate, of which Rh(II,II)/Rh(II,III) redox potential is 0.15 V in acetonitrile (vs. SCE))[7], bridged by the ligands pyz, 4,4'-bpy, and dabco and their oxidized ones.



L = pyz, 4,4'-bpy, and dabco

SCHEME 1

## EXPERIMENTAL

### Preparations

Rhodium(II) acetamidate was prepared by a method described in the literature[8]. The polymer complexes were synthesized by reacting the acetamidate salt with excess of the ligands pyz, 4,4'-bpy, and dabco in acetonitrile under argon at room temperature, the resultant precipitate being filtered out, washed with benzene, and dried under vacuum. Anal. $[Rh_2(HNOCMe)_4pyz]_n$ (**1**) ; Found: C, 27.48; H, 3.75; N, 15.94%. Calcd for $C_{12}H_{26}N_6O_4Rh_2$: C, 27.80; H, 3.89; N, 16.22%. $[Rh_2(HNOCMe)_4 4,4'\text{-bpy}]_n \cdot 2nH_2O$ (**2**); C, 34.56, H, 3.76, N, 13.17%. Calcd for $C_{18}H_{24}N_6O_4Rh_2$: C, 34.30, H, 4.48, N, 13.33%. $[Rh_2(HNOCMe)_4dabco]_n$ (**3**) ; C, 30.55; H, 4.90; N, 15.10%. Calcd for $C_{14}H_{28}N_6O_4Rh_2$: C, 30.56; H, 5.13; N, 15.27%. The yields (based on the dimer) were 84 % for **1**, 81 % for **2**, and 85 % for **3**. Doping reactions were performed for **1**—**3** in acetonitrile using nitrosonium tetrafluoroborate ($NOBF_4$) as oxidant in a similar way as that in the literature[3]. The oxidized dimer $[Rh_2(HNOCMe)_4(MeCN)_2]BF_4$ was prepared by the reaction of the acetamidate salt and $NOBF_4$. The yield was 78%. Anal. Found: C, 23.81; H, 3.50; N, 14.15%. Calcd: C, 23.75; H, 3.65; N, 13.85%.

Measurements

Elemental analyses for carbon, hydrogen, and nitrogen were done using a Yanaco CHN CORDER MT-5. Infrared spectra (KBr pellets) and electronic spectra were measured with JASCO IR-700 and Shimadzu UV-3100 spectrometers, respectively. The magnetic susceptibilities were measured by a Farady method over the temperature range of 5—300 K. The susceptibilities were corrected for diamagnetism of constituent atoms using Pascal's constant[9]. Electrical resistivities were measured for compacted pellets by the conventional two-probe method[10].

## RESULTS AND DISCUSSION

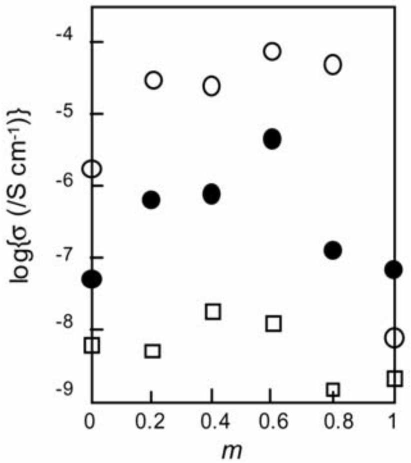


FIGURE 1 Electrical conductivities of the pellets at room temperature for $[Rh_2(HNOCMe)_4L]_n(BF_4)_{mn}$, L = pyz (E), 4,4'-bpy (J), and dabco (G).

Elemental analyses of the obtained complexes showed a stoichiometry $[Rh_2(HNOCMe)_4]$ : L = 1:1 (L = pyz, 4,4'-bpy, and dabco), which is consistent with the formulae for the polymer $[Rh_2(HNOCMe)_4L]_n$. In the IR spectra, the bands of parent dimer $[Rh_2(HNOCMe)_4]$ are all observed at nearly the same wavenumbers for the polymers **1**—**3**. In the diffuse reflectance spectra, absorption band at 580 nm for $[Rh_2(HNOCMe)_4]$ was blue-shifted due to the axial coordination and appeared around 510 nm (for **1**), 480 nm (for **2**), and 500 nm (for **3**). From these results, it was assumed that the objective polymer structure formed on the present reaction. Doping of the obtained polymers **1**—**3** was performed using $NOBF_4$ as oxidant. The ratio (*m*) of the employed mole amount of the oxidant to that of the dimer for each polymer was changed with *m*= 0.2, 0.4, 0.6, 0.8, and 1.0, where the oxidized ones are described by $[Rh_2(HNOCMe)_4L]_n(BF_4)_{mn}$. The *m* values were identified by elemental analyses. The dependence of electrical conductivity on the ratio *m* is displayed in Figure 1. The oxidation of **1** and **2** increased their conductivities by a factor of $10^2$~$10^3$ in S $cm^{-1}$, which, however, decreased again when they were fully oxidized ($m = 1$). In the case of **3**, such an increase was not observed. The difference may come from the lack of the π-system within the ligand dabco although pyz and 4,4'-bpy have the π-system. Interestingly, the same conductive behaviors depending on *m* were obtained for the samples prepared in acetonitrile by mixing Rh(II,II) and Rh(II,III) dimers in the presence of bridging ligands with mole ratios $[Rh_2(HNOCMe)_4]$ : $[Rh_2(HNOCMe)_4]BF_4$: L = 1-*m* : *m* : 1.2. The samples prepared in this manner without bridging ligand revealed the σ values (= ca. $10^{-9}$ S $cm^{-1}$) as the insulator over the range of $m = 0$—1.

The magnetic measurements were performed for the polymers $[Rh_2(HNOCMe)_4L]_n(BF_4)_n$, which correspond to the fully oxidized polymer species ($m = 1$ ) and hereafter are named as **1'** (L = pyz), **2'** (L = 4,4'-bpy), and **3'** (L = dabco), respectively[11]. Temperature dependence of magnetic moments is displayed for **1'** in Figure 2. The magnetic moment at room temperature is 1.71 B.M. (per the dimer). The decrease in the moment is very slight with decreasing the temperature till ca. 10 K, which is indicative of the weak magnetic interaction between the cation dimers. The temperature–dependent profiles of **1'**—**3'** were practically the same and simulated using the equation introduced by Bonner and Fisher for the chain of $S = 1/2$[9]. The parameters obtained in the simulation are listed in Table 1, which indicates that the π systems within the pyz and 4,4'-bpy ligands cannot work effectively for the interaction because there is not any significant difference in the *J* values.

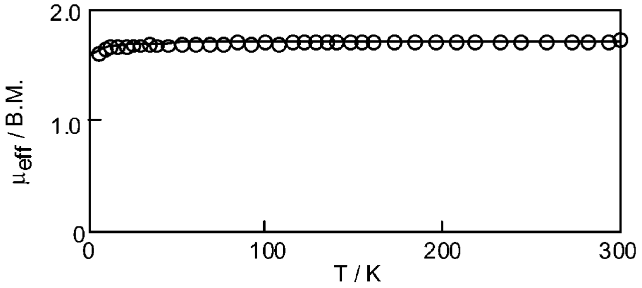


FIGURE 2 Temperature dependence of magnetic moments of **1'**. The solid line was calculated with the parameters in Table 1.

TABLE 1 Fitting Parameters for the Magnetic Data

| | 1Õ | 2Õ | 3Õ |
|---|---|---|---|
| $g$ | 1.97 | 1.99 | 2.07 |
| $J$ / cm$^{-1}$ | -0.3 | -0.5 | -0.3 |

Single crystals of $[Rh_2(HNOCMe)_4(py)_2]BF_4$ were obtained from the pyridine solution. The X-ray analysis[12] showed that the crystal contains two crystallographically independent dimeric cations, one of which is depicted in Figure 3. Crystallographic inversion centers are located at the midpoints of the Rh-Rh bonds of the cationic units. The dihedral angle between the mean plane formed by four equatorial atoms around the rhodium atom and that for the pyridine molecule is close to 90° in each dimeric unit (91.1° for Rh1 and 82.2° for Rh2). If the pyrazine and pyridine (of 4,4'-bpy) rings adopt similar dihedral angle values on the axial coordination in **1'** and **2'**, the weak magnetic interaction can be reasonably interpreted by taking into account that the unpaired electron resides in δ* orbital extended on the equatorial plane[13].

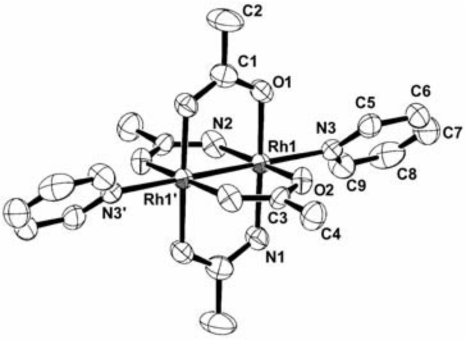


FIGURE 3 ORTEP view of $[Rh_2(HNOCMe)_4(py)_2]^+$. Selected bond distances (Å) are Rh1-Rh1' 2.434(1), Rh1-O1 2.011(5), Rh1-O2 2.046(5), Rh1-N1 2.003(6), Rh1-N2 1.998(7), Rh1-N3 2.215(6), Rh2-Rh2' 2.436(1), Rh2-O3 2.022(5), Rh-O4 2.044(6), Rh2-N4 2.006(7), Rh2-N5 1.992(7), Rh-N6 2.227(6).

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[12.] Crystal data: $C_{18}H_{26}O_4N_6Rh_2BF_4$, formula weight = 683.06, orthorhombic, space group Pcca (no. 54), $a$ = 15.5471(8), $b$ = 19.903(1), $c$ = 16.4731(8) Å, $V$ = 5097.3(8) Å$^3$, $Z$ = 8, $D_{\text{calcd}}$ = 1.78 g/cm$^3$, $R$ ($R_w$) = 0.046 (0.046) for 2918 diffraction data with $I > 3\sigma(I)$ and 316 variables. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-$K\alpha$ radiation.

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