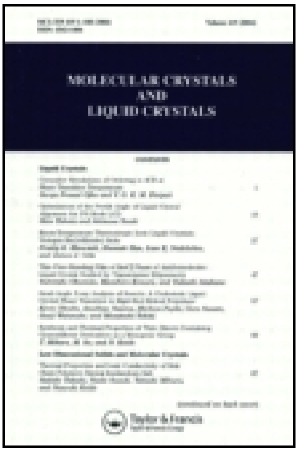

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Coordination Polymers of Ruthenium(II) Acetate with Pyrazine, 4,4′-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane

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Coordination Polymers of Ruthenium(II) Acetate with Pyrazine, 4,4′-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane

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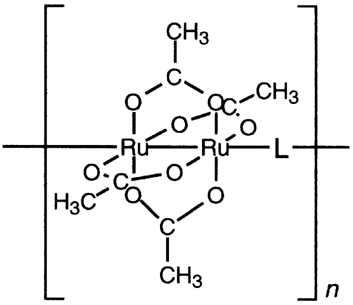
A seires of polymer complexes of ruthenium(II) acetate dimers bridged by pyrazine (pyz), 4,4'-bipyridine (4,4'-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco) were prepared and characterized by elemental analysis, infrared and diffuse reflectance spectroscopy, variable temperature magnetic susceptibility, and electrical conductivity. The significant interdimer interaction through the bridging ligands was not observed for the polymers.

Keywords: polymer complexes; ruthenium(II) acetate; pyrazine; 4,4'-bipyridine; 1,4-diazabicyclo[2.2.2]octane

INTRODUCTION

Much interest is currently devoted to coordination polymers due to their potential applications in catalysis, magnetic and conductive materials, and non-linear optical materials[1]. We have been preparing the polymer complexes comprised of metal carboxylate dimers and linkage ligands $[M_2(O_2CR)_4(L)]_n$ (M = Cu(II), Mo(II), and Rh(II); L = pyrazine (pyz), 4,4'-bipyridine (4,4'-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco)). In the case of Mo(II) and Rh(II), the prepared polymer complexes were all diamagnetic by maintaining the diamagnetic dimer core structure with a metal-metal bond on the axial coordination of the ligands[2]. On the other hand, the polymers of copper(II) carboxylates are paramagnetic because the dimers themselves are paramagnetic for lack of strong interaction coming from the direct metal-metal bond within the dimer core. However, in this case, the unpaired electrons are accommodated in dx^2-y^2 orbitals, which is unfavorable for the interaction between the dimers through the axial ligand. Ruthenium(II,III) carboxlates possess three unpaired electrons in the π^* and δ^* orbitals based on the metal-metal bond and have been ever used to prepare the polymer complexes, which revealed the weak interaction between the ruthenium(II,III) dimers[3]. The investigation on the interdimer interaction was also performed for the ruthenium(II,II) dimer, which has two unpaired electrons in the π* orbitals, using the polymer $[Ru_2(O_2C\text{-}n\text{-}C_{11}H_{23})_4(pyz)]_n$[4], however, not giving conclusive results for presence of the interaction. In this study, we prepared the polymer complexes (Scheme 1) of ruthenium(II) acetate dimers linked by dabco as well as pyz and 4,4'-bpy in order to examine the effect of the ligand π-conjugated system (in pyz and 4,4'-bpy) on the interaction.



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

Scheme 1

EXPERIMENTAL

Preparations

Ruthenium(II) acetate was prepared by a method described in the literature[5]. The acetate salt is air-sensitive and easily oxidized. Hence, the salt was stored under argon in the Schlenck tube and used without weighing accurate amount of the salt employed for the reaction. The salt was mixed with excess of the ligands pyz, 4,4'-bpy, and dabco in benzene under argon and stirred over night at room temperature. The resultant precipitate was filtered, washed with benzene, and dried under vacuum. The obtained polymer complexes were rather stable in the air. Anal. $[Ru_2(OAc)_4(pyz)]_n$ (**1**) ; Found: C, 27.94; H, 3.03; N, 5.22%. Calcd for $C_{12}H_{16}N_2O_8Ru_2$: C, 27.80; H, 3.12; N, 5.40%. $[Ru_2(OAc)_4(4,4'\text{-bpy})]_n$ (**2**); C, 36.22, H, 3.44, N, 4.66%. Calcd for

$C_{18}H_{20}N_2O_8Ru_2$: C, 36.37, H, 3.40, N, 4.71%. $[Ru_2(OAc)_4(dabco)]_n$ (**3**) ; C, 30.07; H, 4.15; N, 4.89%. Calcd for $C_{14}H_{24}N_2O_8Ru_2$: C, 30.55; H, 4.40; N, 5.09%. Doping reactions were performed in benzene for **1**—**3** with ferrocenium tetrafluoroborate as the oxidant in a similar way as that in the literature[6].

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 for **1** and **3** and with a Quantum Design MPMS-5S SQUID susceptomer for **2** at a magnetic field of 0.5 T over the temperature range of 5—300 K. Electrical resistivities were measured for compacted pellets by the conventional two-probe method[7].

RESULTS AND DISCUSSION

Elemental analyses of the obtained complexes showed a stoichiometry $[Ru_2(OAc)_4]$: L=1:1 (L= pyz, 4,4'-bpy, and dabco), which is consistent with the formulae for the polymer $[Ru_2(OAc)_4(L)]_n$. In the IR spectra, the CO_2 vibrations appear as a set of distinctive bands in a similar wavenumber region to those ($\nu_{asym}(CO_2)$ = 1550 cm^{-1}, $\nu_{sym}(CO_2)$ = 1440 cm^{-1}) of the parent dimer $[Ru_2(OAc)_4]$ [5] (TABLE I). The difference between the wavenumbers for the two CO_2 vibration bands, $[\nu_{asym}(CO_2) - \nu_{sym}(CO_2)]$ = 122—128 cm^{-1}, is diagnostic of the bidentate bridging mode for the carboxylate ligands[8]. A slight increase of the values on the polymer formations could be related to the

TABLE I. Infrared and Magnetic Data of **1**—**3**

complex	color	infrared data /cm^{-1}			μ_{eff}(300K)
		ν_{asym} (CO_2)	ν_{asym} (CO_2)	Δ (ν_{asym} -ν_{asym})	/B.M.
1	purple	1560	1438	122	2.88
2	purple	1562	1438	124	2.85
3	brown	1560	1432	128	2.91

axial coordination.

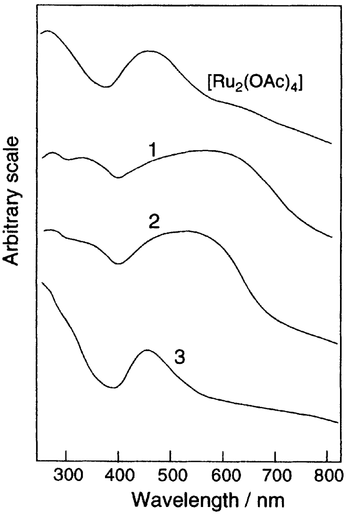


FIGURE 1. Reflectance Spectra of **1**—**3** and [$Ru_2(OAc)_4$].

The diffuse reflectance spectra of **1**—**3** are shown with that of [$Ru_2(OAc)_4$] in FIGURE 1. The π-π^* transition band based on the metal-metal bond in the dimer core of [$Ru_2(OAc)_4$] is shifted to the longer wavelength region in **1** and **2**. The spectral shapes are indicative of presence of shoulder bands around 500 nm. Such a shift has been observed in toluene for the coordination of pyz to a Ru(II,II) dimer with long chain caboxylates[9].

The room temperature magnetic moments of **1**—**3** are 2.85—2.91 B.M. (TABLE I), which indicates that they have two unpaired electrons per Ru_2 unit as has been reported for the other ruthenium(II,II) carboxylates and their adduct complexes[10,11]. Temperature dependence of magnetic moments are displayed for **1** and **3** in FIGURE 2. The magnetic moments are both decreased constantly with lowering temperature. The temperature-dependent profiles of **1**—**3** are practically the same and fully explained by the equation for the $S = 1$ system in consideration of zero-field splitting[12] without any parameters concerning the interdimer interaction. The parameters obtained by the simulation (see solid lines in FIGURE 2) are as follows: $D = 290$ cm^{-1}, $g = 2.19$, $\rho = 0.07$, $R = 4.09\times10^{-4}$ for **1**; $D = 270$ cm^{-1}, $g = 2.15$, $\rho = 0.05$, $R = 1.69\times10^{-4}$ for **2**; $D = 260$ cm^{-1}, $g = 2.19$, $\rho = 0.07$, $R = 1.29\times10^{-4}$ for **3**[13]. The g and D values are similar to those reported for the ruthenium(II) caboxylates[10]. The present results suggest that the interdimer interaction is negligibly small compared with the zero-field splitting and does not affect the bulk behavior in magnetism even if the linkage ligand has the conjugated π-system. In the case of coordination polymers of ruthenium(II,III) acetate dimers bridged by pyz and 4,4'-bpy, the interaction was reported not to be negligible ($zJ = -2.3$ cm^{-1} for pyz polymer and -1.0 and -0.65 cm^{-1} for 4,4'-bpy polymers)[3]. It was concluded that the π-system in the ligand plays a

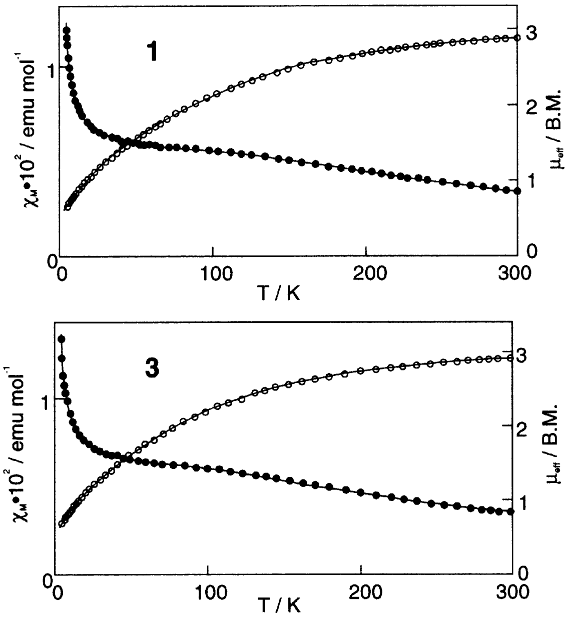


FIGURE 2. Temperature dependences of the magnetic susceptibilities (●) and magnetic moments (○) for **1** (upper side) and **3** (lower side). The solid lines were calculated with the parameters in the text.

certain role in mediating the interaction because the dabco polymer showed a smaller interaction (zJ = -0.59 cm^{-1}) though the interdimer distance through the ligand is similar to that for the pyz polymer[3b]. The difference between Ru(II,II) and Ru(II,III) polymers could be due to the fact that the zero-field splitting of Ru(II,III) dimer (D = ~60 cm^{-1}) is much smaller in magnitude than that of Ru(II,II) dimer.

Room temperature conductivities revealed that **1**—**3** are all insulators (σ = ~10^{-10} S cm^{-1}). The doping with the oxidant ferrocenium tetrafluoroborate gave rise to an increase in the conductivity up to σ = 10^{-6} ~ 10^{-7} S cm^{-1} for each polymer until completing the oxidation of Ru(II,II) to Ru(II,III) in the polymer; σ = ~10^{-8} S cm^{-1} when fully oxidized. However, there was no important difference in the conducting behavior among the polymers with L = pyz, 4,4'-bpy, and dabco, which implies that the origin of the relatively high conductivities could not be through the bridging ligands. Details are now under investigation.

After submission of this paper, an analogous polymer complex has been very recently reported[14].

Acknowledgment

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References

[1] For example, see D. J. Chesnut, D. Hagrman, P. J. Zapf, R. P. Hammond, R. LaDuca, R.C. Haushalter, and J. Zubieta, *Coord. Chem. Rev.*, **190-192**, 737 (1999).

[2] M. Handa, M. Watanabe, D. Yoshioka, S. Kawabata, R. Nukada, M. Mikuriya, H. Azuma, and K. Kasuga, *Bull. Chem. Soc. Jpn.*, **72**, 2681 (1999) and references therein.

[3] a) F. D. Cukiernik, A.-M. Giroud-Godquin, P. Maldivi, and J.-C. Marchon, *Inorg. Chim. Acta*, **215**, 203 (1994); b) E. J. Beck, K. D. Drysdale, L. K. Thompson, L. Li, C. A. Murphy, and M. A. S. Aquino, *Inorg. Chim. Acta*, **279**, 121 (1998).

[4] L. Bonnet, F. D. Cukiernik, P. Maldivi, A.-M. Giroud-Godquin, and J.-C. Marchon, *Chem. Mater.*, **6**, 31 (1994).

[5] A. J. Lindsay, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, **1985**, 2321.

[6] J. P. Collman, J. T. McDevitt, C. R. Leidner, G. T. Yee, J. B. Torrance, and W. A. Little, *J. Am. Chem. Soc.*, **109**, 4606 (1987).

[7] S. Araki, H. Ishida, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **51**, 407 (1978).

[8] K. Nakamoto, "*Infrared and Ramn Spectra of Inorganic and Coordination Conpounds*," 4th ed, Wiley Interscience, New York (1986).

[9] J. L. Wesemann and M. H. Chisholm, *Inorg. Chem.*, **36**, 3258 (1997).

[10] M. A. S. Aquino, *Coord. Chem. Rev.*, **170**, 141 (1998).

[11] F. A. Cotton and R. A. Walton, "*Multiple Bonds between Metal Atoms*," 2nd ed, Oxford Univ. Press, New York (1993).

[12] C. J. O'Connor, *Prog. Inorg. Chem.*, **29**, 203 (1982).

[13] ρ = fraction of impurity ($S = 1/2$); $R = \Sigma(\chi_{obs} - \chi_{calcd})^2/\Sigma\chi_{obs}^2$.

[14] H. Miyasaka, R.Clérac, C. S. Campos-Fernández, and K. R. Dunbar, *J. Chem. Soc., Dalton Trans.*, **2001**, 858.