Polymer Complexes of Rhodium(II) Trifluoroacetamidate with Pyrazine, 4,4′-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane

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Polymer complexes of rhodium(II) trifluoroacetamidate dimers bridged by bidentate ligands $[\{Rh_2(HNOCCF_3)_4(L)\}_n]$, L = pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco), have been prepared and characterized.

Although many ligand-bridged polymers of tetra-μ-carboxylato-dimetal complexes ($[M_2(O_2CR)_4]^{+/0}$) have been presented, similar polymers of tetra-μ-amidato-dimetal complexes ($[M_2(HNOCR)_4]^{+/0}$) are very limited in number.[1] Recently, chain complexes of rhodium(II,III) acetamidate dimers with halogen bridges, $[\{Rh_2(HNOCMe)_4X\}_n]$, X = Cl and Br, have been presented.[2] To our knowledge, there has been no report on the polymer complexes of rhodium(II,II or II,III) amidate dimers ($[Rh_2(HNOCR)_4]^{+/0}$) bridged by the bidentate ligands such as pyrazine (pyz). We have lately reported on the polymers of rhodium acetamidate dimers with the bidentate ligands, pyrazine, 4,4′-bipyridine (4,4′-bpy), and 1,4-diazabicyclo[2.2.2]octane (dabco).[3] It is important to accumulate the data on the properties of the polymer complexes of the amidate dimers by changing the substituent on the amidate ion in order to estimate the potentiality of the dimers as building blocks in combination with linkage ligands. In the present study, we prepared and characterized polymer complexes of rhodium(II) trifluoroacetamidate dimers $[\{Rh_2(HNOCCF_3)_4(L)\}_n]$ (L = pyz, 4,4′-bpy, and dabco), the X-ray structure analysis being performed for the 4,4′-bpy complex.

Based on the elemental-analytical data, the complexes obtained by reacting the dimer and the bridging ligands in methanol were identified as the formulae $[\{Rh_2(HNOCCF_3)_4(pyz)\}_n]\cdot n$MeOH (**1**·$n$MeOH), $[\{Rh_2(HNOCCF_3)_4(4,4'\text{-bpy})\}_n]\cdot n$MeOH (**2**·$n$MeOH), and $[\{Rh_2(HNOCCF_3)_4(dabco)\}_n]\cdot n$MeOH (**3**·$n$MeOH). Diffuse reflectance spectra of **1**·nMeOH–**3**·nMeOH are shown with that of their parent dimer $[Rh_2(HNOCCF_3)_4]$ in Fig. 1. The absorption at 595 nm for $[Rh_2(HNOCCF_3)_4]$ is shifted to the shorter wavelength region and appears as a shoulder band around 470 nm for **1**·nMeOH and **2**·nMeOH and as a peak at 495 nm for **3**·nMeOH. Such blue-shifts can be explained by the axial interaction caused by the coordination of the bridging ligands as in the case of rhodium(II) carboxylate dimers with axial ligands.[4,5] The π-interaction in addition to the σ-interaction at the axial positions could be the reason for the larger blue-shifts for **1**·nMeOH and **2**·nMeOH.[5]

The crystal structure of **2** is depicted in Fig. 2. The crystallographic inversion center is located at the center of the dimer core. It is clearly seen that the chain structure is built up by the alternating arrangement of the Rh_2 dimer and 4,4′-bpy. In Table 1, Rh–Rh and axial bond (Rh–N_{ax}) lengths for **2** are listed with those for 4,4′-bpy or pyridine adducts of rhodium(II) caboxylate or amidate dimers.[6–9] It is usual that the Rh–Rh distances (2.437(1)–2.472(3) Å) of the amidate dimers are considerably longer than those for the carboxylate dimers (2.396(2) and 2.395(1) Å).[1] The relatively long Rh–Rh distances of $[Rh_2(HNOCCF_3)_4(py)_2]$ and **2** compared with that of $[Rh_2(HNOCPh)_4(py)_2]$ are attributable to the enhanced axial interaction by the higher metal acidity due to the electron-withdrawing fluorine atoms within the $Rh_2(HNOCCF_3)_4$ dimer core. The quite long Rh–N_{ax} distances (2.26(1) and 2.31(1) Å) of $[Rh_2(HNOCCF_3)(py)_2]$ might be related to the problem described in the literature;[6] the authors encountered a difficulty in determining the axially coordinated atoms during the X-ray analysis of $[Rh_2(HNOCCF_3)(py)_2]$. The other complexes have similar Rh–N_{ax} distances around 2.225 Å except for one of the bonds of $[\{Rh_2(O_2CCMe_3)_4(4,4'\text{-bpy})\}_n]$ (2.264(5) Å). Two pyridine rings of 4,4′-bpy in **2** are coplanar. This is in contrast with the case of $[\{Rh_2(O_2CCMe_3)_4(4,4'\text{-bpy})\}_n]$, of which the dihedral angle between the ring planes is 38.2(3)°.[9] In the previous study, we pointed out that crystal solvent molecules exist for filling the space in the crystal when the two pyridine rings are coplanar in the polymers of the carboxylate dimers and the

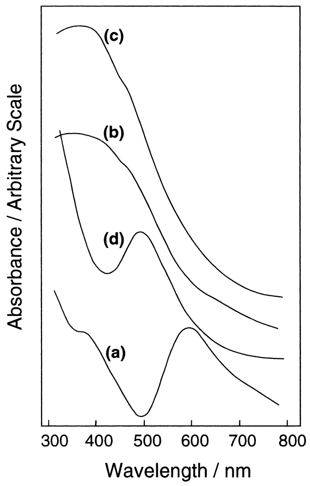

Fig. 1. Diffuse reflectance spectra of $[Rh_2(HNOCCF_3)_4]$ (a), **1**·nMeOH (b), **2**·nMeOH (c), and **3**·nMeOH (d).

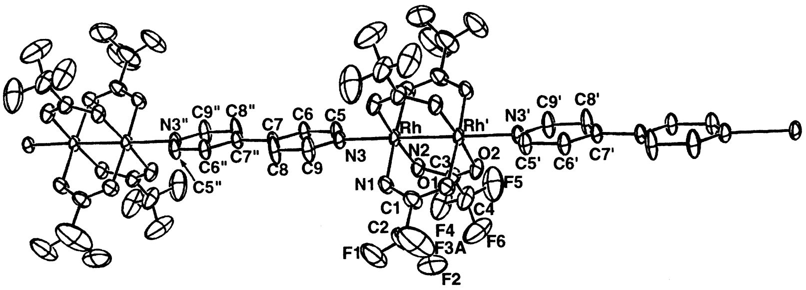

Fig. 2. Polymer structure of **2**. Unprimed, primed, and double-primed atoms are related by the inversions. Selected bond distances (Å) and angles (°); Rh–Rh′ 2.456(1), Rh–O1′ 2.058(4), Rh–O2′ 2.069(4), Rh–N1 2.002(5), Rh–N2 1.992(5), Rh–N3 2.222(4), Rh–Rh′–O1 89.4(1), Rh–Rh′–O2 89.3(1), Rh′–Rh–N1 85.9(1), Rh′–Rh–N2 85.7(1), Rh′–Rh–N3 178.4(1).

Table 1. Rh–Rh and Rh–Axial Ligand Bond Lengths of 4,4′-bpy or Pyridine Adducts of Rhodium(II) Dimers

Complexes	Rh–Rh	Rh–N_{ax}	Ref.
$[Rh_2(HNOCCF_3)(py)_2]$	2.472(3)	2.26(1), 2.31(1)	6
$[Rh_2(HNOCCF_3)_4(4,4'\text{-bpy})]_n$ (**2**)	2.456(1)	2.222(4)	This work
$[Rh_2(HNOCPh)_4(py)_2]$	2.437(1)	2.227(7)	7
$[Rh_2(O_2CMe)_4(py)_2]$	2.3963(2)	2.227(3)	8
$[\{Rh_2(O_2CCMe_3)_4(4,4'\text{-bpy})\}_n]$	2.395(1)	2.225(5), 2.264(5)	9

4,4′-bpy linkage ligand.[9] It is interesting that the complex **2** has a coplanar orientation of the pyridine rings of 4,4′-bpy without crystal solvents.

Experimental

Preparation. $[Rh_2(HNOCCF_3)_4]$ was prepared by a similar way to that described in the literature.[6] Polymer complexes **1**·*n*MeOH–**3**·*n*MeOH were prepared by reacting the parent dimer (0.13 mmol) and the corresponding ligand (0.28 mmol) pyz, 4,4′-bpy, or dabco in methanol. They are obtained as yellow (for **1**·*n*MeOH and **2**·*n*MeOH) and pink (for **3**·*n*MeOH) microcrystals. The yield were 60–70% (based on the dimetal unit). Anal. **1**·*n*MeOH; Found: C, 20.33; H, 1.26; N, 10.14%. Calcd for $C_{12}H_{12}F_{12}N_6O_5Rh_2$: C, 20.38; H,1.58; N, 10.44%. **2**·*n*MeOH; C, 27.24, H, 1.59, N, 9.66%. Calcd for $C_{19}H_{16}F_{12}N_6O_5Rh_2$: C, 27.10, H, 1.61, N, 9.98%. **3**·*n*MeOH; C, 22.73; H, 2.20; N, 10.03%. Calcd for $C_{15}H_{20}F_{12}N_6O_5Rh_2$: C, 22.57; H, 2.53; N, 10.53%.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanaco CHN CORDER MT-5. Electronic spectra were measured with a Shimadzu UV-3100 spectrometer.

X-ray Crystal Structure Analysis. Crystals of **2** were obtained by slow diffusion technique using an H-shaped tube in a mixed solvent of methanol and benzene. The procedure of the X-ray analysis is described elswhere. There is a disorder at a fluorine atom of the acetamidate ion, which is divided into two positions with the same weight (F3A corresponds to one of them in Fig. 2). The hydrogen atoms were inserted at their calculated positions and fixed there. The calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.

Crystallographic data: $C_{18}H_{12}F_{12}N_6O_4Rh_2$, Fw = 810.12, monoclinic, space group *C2/c*, $a = 17.219(5)$, $b = 19.314\ (2)$, $c = 8.755(3)$ Å, $\beta = 108.82(1)$, $V = 2756(1)$ Å^3, $Z = 4$, $D_m = 1.93$, $D_c = 1.95$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 12.93$ cm^{-1}, $F(000) = 1568$, crystal dimensions 0.35×0.31×0.22 mm, 2508 reflections collected, 1739 independent reflections, $R\ [I \geq 3\sigma(I)] = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.034$, $R_w\ [I \geq 3\sigma(I)] = [\Sigma w(|F_o|-|F_c|)^2/\Sigma|F_o|^2]^{1/2} = 0.038$.

The X-ray analysis data have been deposited as Document No. 75035 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers CCDC 185487.

References

1 F. A. Cotton and R. A. Walton, "Multipule Bonds between Metal Atoms," 2nd ed, Oxford Univ. Press, New York (1993), pp.399–430.

2 Z. Yang, T. Fujinami, M. Ebihara, K. Nakajima, H. Kitagawa, and T. Kawamura, *Chem. Lett.*, **2000**, 1006; Z. Yang, M. Ebihara, T. Kawamura, T. Okubo, and T. Mitani, *Inorg. Chim. Acta*, **321**, 97 (2001).

3 M. Handa, Y. Muraki, S. Kawabata, T. Sugimori, I. Hiromitsu, M. Mikuriya, and K. Kasuga, *Mol. Cryst. Liq. Cryst.*, in press.

4 K. M. Kadish, D. Lancon, A. M. Dennis, and J. L. Bear, *Inorg. Chem.*, **21**, 2987 (1982).

5 R. S. Drago, J. R. Long, and R. Cosmano, *Inorg. Chem.*, **20**, 2920 (1981).

6 A. M. Dennis, J. D. Korp, I. Bernal, R. A. Howard, and J. L. Bear, *Inorg. Chem.*, **22**, 1522 (1983).

7 A. R. Chakravarty, F. A. Cotton, D. A. Tocher, and J. H. Tocher, *Inorg. Chim. Acta*, **101**, 185 (1985).

8 Y. B. Koh and G. G. Christoph, *Inorg. Chem.*, **17**, 2590 (1978).

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