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Mixed Chromium(III)-Ruthenium(III) Trinuclear Complex, $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(pyridine)_3]^+$

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A mixed Cr-Ru trinuclear complex $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$ has been prepared, which is the first example of mixing two metal ions of both different rows and groups into the trinuclear unit. Its magnetic and redox behavior indicate that d^3 Cr(III) ion acts as if isolated ion, and that two d^5 Ru(III) ions are effectively coupled while the Cr-Ru interaction is less significant as compared with the Ru-Ru one.

One of the important approaches to elucidate metal-metal interactions in polynuclear complexes is to prepare mixed-metal complexes and examine their various properties.1) The trinuclear complexes, $[M_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ (L: neutral unidentate ligand), provide a unique opportunity for studying hetero-metal interactions systematically, since they are known for a wide variety of tervalent metal ions2) such as V, Cr, Mn, Fe, Ru, Rh, and Ga,3) and yet structural characteristics such as metal-metal and metal-O(μ_3) distances are very similar among the complexes of various metal ions.2) Mixed metal complexes were limited, however, to those between metal ions of the first-row transition elements2) except for mixed Ru-Rh complexes, $[RhRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]^+$ (L = H_2O or pyridine (py)).1b) Earlier studies4,5) indicated that metal-metal interaction through the central oxide ion is much stronger for the Ru complexes than for those of the first-row transition elements, and the properties of the $RhRu_2$ complexes were interpreted in terms of the molecular orbital based on $d\pi$(Rh, Ru)-$p\pi$(μ_3-O) interaction.1b) Since such a type of MO interaction is virtually absent for the complexes of first-row transition elements, we thought that it would be important to see if stable mixed-metal complexes are formed between first- and second-row transition elements, and also how the $d\pi$-$p\pi$ interaction is affected. We wish to report here a new mixed Cr-Ru complex, $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$, which is the first example of a trinuclear complex containing two kinds of metal ions with both different rows and groups.

$RuCl_3 \cdot nH_2O$ (250 mg) and $Cr(CH_3COO)_3$ (250 mg) were dissolved in a mixture of water(30 cm^3)-acetic acid(40 cm^3)-ethanol(10 cm^3), and the solution was refluxed for 1 h. The products were then separated and purified by treatment with a cation-exchange column (3 cm ϕ, 60 cm x 4) of Dowex 50W-X2 in the Na^+ form. On elution with 0.01 M $NaClO_4$ - 0.01 M $HClO_4$ (1 M = 1 mol^{-1} dm^{-3}), the violet eluate of $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ (1000 - 1500 cm^3) was preceded by the green eluate of $[Cr_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$

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and followed by the blue eluate of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$. After the violet eluate was rotoevaporated to 10 cm^3, ca. 10 cm^3 of pyridine was added, and then the solution was kept at ca. 80 °C for 30 min. A violet powder of $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]ClO_4$ was obtained on cooling, which was collected by filtration and washed with water and ethanol. This was recrystallized from CH_2Cl_2-ethanol solution. Yield, ca. 40 mg.6) The behavior of the column chromatography and analytical data6) provide unambiguous evidence for the formation of the $CrRu_2$ complex. The pyridine complex and corresponding aqua complex7) are surprisingly stable in acetonitrile and aqueous acidic solution, respectively, and can be stored without decomposition for more than a few weeks.

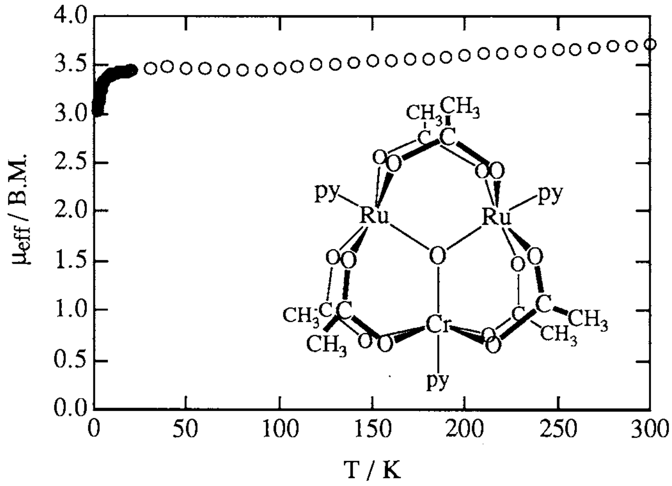

Fig. 1. Proposed structure and the magnetic moment ($\mu_{eff} = 2.828\ (\chi_m T)^{1/2}$) of $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]PF_6$ as a function of temperature.

There is no experimental evidence for the formation of the Cr_2Ru complex. We also noted that the M_2Ru complex was not formed in the preparation of the mixed Rh-Ru complexes.1b) We have demonstrated that the dimeric species with the $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ core is very likely to be formed in an early stage of the preparation and to act as a precursor to the mixed metal complexes.8)

Figure 1 shows the magnetic moment ($\mu_{eff} = 2.828(\chi_m T)^{1/2}$) of $[CrRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]PF_6$ as a function of temperature.9) The magnetic moment is essentially temperature independent in the range above ca. 20 K and its value of 3.5 B.M. is close to the spin only value of d^3 Cr(III) ion. It appears as if Cr (III) behaves as an isolated ion and the two d^5 Ru(III) ions are effectively coupled in the trinuclear core. The magnetic behavior indicates that the MO type interaction suggested for the $RhRu_2$ complex1b) is not applicable to the $CrRu_2$ complex as far as the Cr-Ru interaction is concerned. Such difference appears to be reflected in the electronic absorption spectrum.10) A sharp drop of μ_{eff} below 20 K is not easily explained by such a simple model11) and suggests weak magnetic interactions among Cr(III) and Ru(III) ions in the trinuclear cluster core.

A cyclic voltammogram of the new complex in CH_3CN is shown in Fig. 2 along with that of $[RhRu_2(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]ClO_4$. The $CrRu_2$ complex shows three reversible waves at +1.64, +0.78, and -0.68 V vs. Ag/Ag^+. They are confirmed to be all one-electron processes by comparing peak current intensities with those of $RhRu_2$ complex. All the redox potentials of the $CrRu_2$ complex are very similar to those of the corresponding potentials of the $RhRu_2$ complex. This shows that the redox processes of the two complexes are essentially localized at the Ru_2O moiety. Although the extent of Cr-Ru and Rh-Ru interactions is different (vide supra), such difference appears to be less influential to the redox potentials of the Ru_2O moiety.

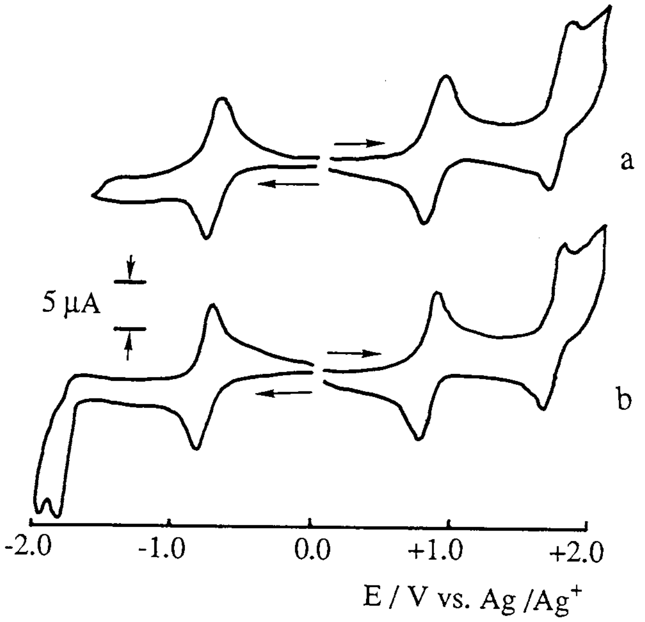

Fig. 2. Cyclic voltammogram of [$CrRu_2(\mu_3$-O)(μ-$CH_3COO)_6(py)_3](ClO_4)$ (a) and [$RhRu_2(\mu_3$-O)(μ-$CH_3COO)_6(py)_3](ClO_4)$ (b) in 0.1 M (n-$C_4H_9)_4NClO_4$-CH_3CN solution. Glassy carbon working-, Pt coil auxiliary-, and Ag/Ag$^+$ ([$AgClO_4$] = 0.1 M) reference-electrodes were used at a scan rate of 50 mV / s.

We are currently trying to prepare other mixed-metal complexes of the Ru_2M type in order to develop a more general understanding of the metal-metal interactions in this type of complexes.

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6) Anal. Found: C, 33.32; H, 3.76; N, 4.64; Cl, 3.84%. Calcd for $C_{27}H_{33}N_3O_{17}ClCrRu_2$: C, 33.74; H, 3.46; N, 4.37; Cl, 3.69%. M/Z (FAB-MASS)= 863. The XPS spectrum showed that the complex contains both chromium and ruthenium in 1:2 ratio as determined from the integrated peak intensities of Ru-3p and Cr-2p peaks. A preliminary study on the Ru K-edge EXAFS is consistent with the trinuclear structure.
7) The corresponding aqua complex can be isolated from the concentrated eluate before addition of pyridine, but it is difficult to obtain a sufficient amount of pure sample.
8) Y. Sasaki, M. Suzuki, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, and T. Ito, *J. Am. Chem. Soc.*, **110**, 6251 (1988); Y. Sasaki, M. Suzuki, A. Nagasawa, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, T. Ochi, and T. Ito, *Inorg. Chem.*, **30**, 4903 (1991).
9) SQUID (Quantum Design Magnetic Measurement System) method. Data in the low temperature region show the compound is almost free from paramagnetic impurities.
10) The $CrRu_2$ complex shows three distinctive peaks at 665 (ε = 1400 cm^{-1} $mol^{-1}dm^3$), 525 (2900), and 241 nm (15000). The spectral pattern is appreciably different from those of the Ru_2Rh and Ru_3 complexes. The two visible absorption bands of the $CrRu_2$ complex should correspond to the transitions between the orbitals derived from mainly Ru dπ and μ_3-O pπ interaction.
11) H. Kobayashi, N. Uryû, A. Ohto, Y. Sasaki, and T. Ito, Details will be reported elesewhere.

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