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Mixed-Metal Trinuclear Complexes Containing Two Ruthenium(III) Ions and a Divalent Metal Ion, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]$ (M = Mg, Mn, Co, Ni, Zn; L = H_2O, Pyridine)

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Oxo-centered trinuclear mixed-metal complexes, $[M_2M'(\mu_3\text{-}O)(\mu\text{-}RCOO)_6(L)_3]^{n+}$ (hereafter abbreviated as M_2M'; L = neutral unidentate ligand), have played an important role in understanding the nature of metal–metal interaction, in particular magnetic properties of first-row transition elements.[1] Complexes are known for the series, Fe_2M', Cr_2M', $FeCrM'$ (M′ stands for tri- and divalent metal ion with $n = 1$ and 0, respectively).[2] The ruthenium(III) trinuclear analogs are interesting because they have much stronger metal–metal interaction through the central oxide ion as manifested by strong visible absorption bands and a series of reversible redox processes.[3] Mixed-metal trinuclear complexes containing ruthenium(III) ions are thus important. Only two complexes, Ru_2Rh[4] and Ru_2Cr,[5] are known, however, owing to difficult synthetic procedures. We have found a simple preparative method for mixed-metal trinuclear complexes containing two ruthenium ions and a divalent metal ion. Ten new complexes, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(L)_3]$ (M = Mg, Mn, Co, Ni, Zn; L = H_2O, pyridine(py)), are reported here.

$RuCl_3\cdot nH_2O$ (0.15 g) was dissolved in a mixture of ethanol (20 cm^3), water (10 cm^3), and acetic acid (25 cm^3). The mixture was then heated at 70 °C for 10 min, whereupon the color of the solution changed from brown to red. This red solution most likely contained a ruthenium(III) dimer with a "$Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$" core.[6] After the solution was cooled down to ambient temperature, a corresponding divalent metal acetate (0.50 g) was added to the solution. A red-purple solid of the aqua complex, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]$, precipitated after a few hours to 2 days.[7] Pyridine complexes, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]$, were obtained by the following procedure. A small amount of pyridine (ca. 10 mL) was added to a stirred suspension of the aqua complex (ca. 100 mg) in CH_3CN (ca. 30 mL). The suspension was stirred overnight, and the resulting blue-violet solution was evaporated to dryness. The residue was dissolved in pyridine to give good quality violet crystals of $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]\cdot py$ after 1 month for all the divalent metal ions. All the new compounds gave satisfactory C, H, and N analytical data. The aqua complexes are soluble in water, alcohol, and tetrahydrofuran, but they decompose in a few days. The pyridine complexes are soluble in water and organic solvents.

Pyridine complexes of Ni and Co, $[Ru_2Ni(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]\cdot py$ and $[Ru_2Co(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]\cdot py$, crystallize in the trigonal space group *R*32 with $Z = 3$.[8] The molecular structure of the Ru_2Ni complex is shown in Figure 1. The Ru_2Co complex is isostructural. In both compounds, all metal ions are statistically disordered within the trinuclear core. A 3-fold rotation axis passes through the central O^{2-} ion (O1) perpendicular to the plane of the cluster core, and a 2-fold rotation axis passes through C5, N1, M, and O1. Pyridine ligands are almost coplanar to the cluster core. M···M distances of 3.346(1) Å in Ru_2Ni and 3.359(1) Å in Ru_2Co indicate the absence of direct metal–metal bonding. The coordinated pyridine rings are stacked with pyridine ligands in adjacent complexes and they are related by a 3-fold screw axis. Each complex has a pyridine solvate molecule which lies between two Ru_2M molecules and has its plane perpendicular to the $Ru_2M(\mu_3\text{-}O)$ plane. Each pyridine solvate molecule is 3-fold disordered about the 3-fold rotation axis. Structural parameters of both complexes are very similar to each other and to those for other trinuclear complexes.[9]

The powder magnetic susceptibilities of the pyridine complexes have been measured by using the SQUID method (1.8–300 K). Magnetic moments ($\mu_{eff} = 2.828(\chi_m T)^{1/2}$) per molecule are plotted against temperature in Figure 2.[10] Except for the Co complex, the μ_{eff} values for these complexes are essentially temperature-independent over the temperature range above 20 K and are nearly equal to the spin-only values for the divalent metal ions.

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(1) For example: (a) Long, G. J.; Robinson, W. T.; Tappmeyer, W. P.; Bridges, D. L. *J. Chem. Soc., Dalton Trans.* **1973**, 573. (b) McCusker, J. K.; Jang, H. G.; Wang, S.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 1874.

(2) Blake, A. B.; Yavari, A.; Hatfield, W. E.; Sethylekshmi, C. N. *J. Chem. Soc., Dalton Trans.* **1985**, 2509.

(3) (a) Cotton, F. A.; Norman, Jr., J. G. *Inorg. Chim. Acta* **1972**, *6*, 411. (b) Baumann, J. A.; Salmon, D. J.; Wilson, S. T.; Meyer, T. J.; Hatfield, W. E. *Inorg. Chem.* **1978**, *17*, 3342. (c) Kobayashi, H.; Uryû, N.; Tokiwa, A.; Yamaguchi, T.; Sasaki, Y.; Ito, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 198. (d) Abe, M.; Sasaki, Y.; Yamaguchi, T.; Ito, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1585.

(4) Sasaki, Y.; Tokiwa, A.; Ito, T. *J. Am. Chem. Soc.* **1987**, *109*, 6341.

(5) Sasaki, Y.; Yoshida, Y.; Ohto, A.; Tokiwa, A.; Ito, T.; Kobayashi, H.; Uryû, N.; Mogi, I. *Chem. Lett.* **1993**, 69.

(6) (a) Sasaki, Y.; Suzuki, M.; Tokiwa, A.; Ebihara, M.; Yamaguchi, T.; Kabuto, C.; Ito, T. *J. Am. Chem. Soc.* **1988**, *110*, 6251. (b) Sasaki, Y.; Suzuki, M.; Nagasawa, A.; Tokiwa, A.; Ebihara, M.; Yamaguchi, T.; Ito, T. *Inorg. Chem.* **1991**, *30*, 4903.

(7) In the case of the Fe analog, Ru_2Fe^{III} was isolated from this procedure even though the divalent iron salt $FeCl_2\cdot nH_2O$ was allowed to react with the red solution. Details will be reported.

(8) Crystallographic data for $[Ru_2Ni(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6py_3]\cdot py$ ($C_{32}H_{38}N_4NiO_{13}Ru_2$): fw 947.50, trigonal space group *R*32, $a = 17.492(4)$ Å, $c = 11.078(5)$ Å, $V = 2935(1)$ Å^3, and $D_c = 1.61$ g cm^{-3} for $Z = 3$. Structure solution and refinement were based on 758 unique reflections ($F_o^2 > 3\sigma(F_o^2)$). $R = 0.029$; $R_w = 0.033$. Crystallographic data for $[Ru_2Co(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6py_3]\cdot py$ ($C_{32}H_{38}N_4CoO_{13}Ru_2$): fw 947.75, trigonal space group *R*32, $a = 17.536(5)$ Å, $c = 11.076(6)$ Å, $V = 2949(1)$ Å^3, and $D_c = 1.60$ g cm^{-3} for $Z = 3$; 740 unique reflections ($F_o^2 > 3\sigma(F_o^2)$) were used. $R = 0.026$, $R_w = 0.026$. All measurements for both crystals were made on a Rigaku AFC-5R diffractometer. Data were collected at room temperature with Mo Kα (λ = 0.710 69 Å) radiation using the 2θ–ω scan technique up to 2θ = 55°. No absorption correction was applied, because both complexes have low absorption coefficient for Mo Kα ($\mu = 13.03$ cm^{-1} for Ru_2Ni and $\mu = 12.39$ cm^{-1} for Ru_2Co). Three metal ion sites were statistically disordered in both complexes. The structures were refined under the conditions that occupancy factors and positional and thermal parameters for the metal sites were fixed as the disordered model permits. Hydrogen atoms were ignored in the analyses. All non-hydrogen atoms except for those in the disordered solvate molecule were anisotropically refined. Atomic positional and thermal parameters are provided as a supplementary material. Selected bond distances (Å) and angles (deg) for $[Ru_2Co(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6py_3]\cdot py$ (atom labeling scheme the same as that in Figure 1): M···M = 3.359(1), M–O1 = 1.9394(8), M–O2 = 2.053(3), M–O3 = 2.070(3), M–N1 = 2.174(5); M–O1–M = 120.0, O1–M–O2 = 94.8(1), O1–M–O3 = 94.8(1), O2–M–O3 = 90.0(2), O2–M–N1 = 85.2(1), O3–M–N1 = 85.2(1).

(9) For example, Mn_3: Vincent, J. B.; Chang, H-R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703. Fe_3: Woehler, S. E.; Wittebort, R. J.; Oh, S. M.; Kambara, T.; Hendrickson, D. N.; Strouse, C. E. *J. Am. Chem. Soc.* **1987**, *109*, 1063. Fe_2Co: Jang, H. G.; Kaji, K.; Sorai, M.; Wittebort, R. J.; Geib, S. J.; Rheigold, A. L.; Hendrickson, D. N. *Inorg. Chem.* **1990**, *29*, 3547.

(10) Magnetic measurements were carried out by using a Quantum Design SQUID MPMS susceptometer operating at a magnetic field strength of 5 kG. Corrections for diamagnetism were carried out by using tabulated Pascal constants.

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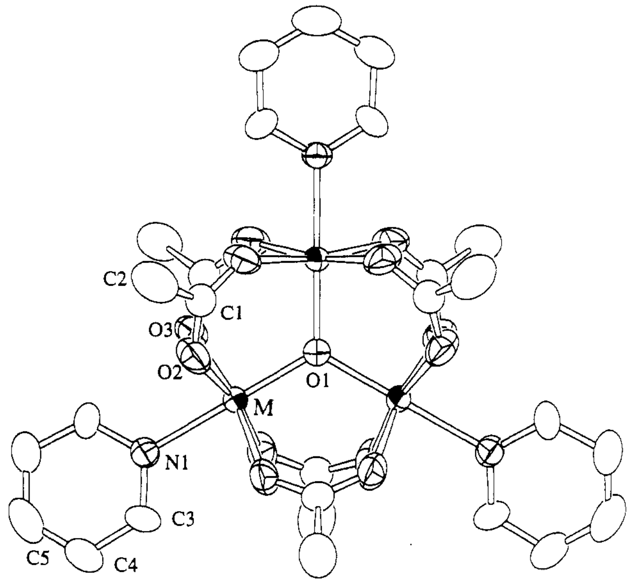

Figure 1. Structure of $[Ru_2Ni(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6py_3]\cdot py$. For clarity, the solvate pyridine molecule is omitted. Selected bond distances (Å) and angles (deg): M···M = 3.346(1), M–O1 = 1.9318(7), M–O2 = 2.052(4), M–O3 = 2.057(4), M–N1 = 2.136(6); M–O1–M = 120.0, O1–M–O2 = 95.0(1), O1–M–O3 = 94.8(1), O2–M–O3 = 90.3(2), O2–M–N1 = 85.0(1), O3–M–N1 = 85.2(1).

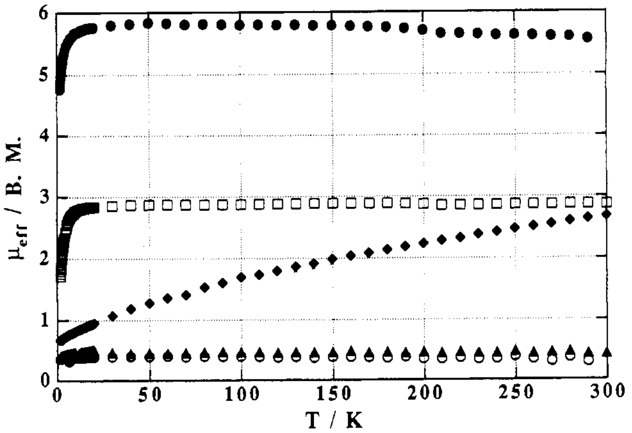

Figure 2. Effective magnetic moment per molecule for the pyridine complexes of Ru_2Mg(▲), Ru_2Mn(●), Ru_2Co(◆), Ru_2Ni(□), Ru_2Zn(○).

At very low temperature, Ru_2Mn and Ru_2Ni display sharp decreases in the μ_{eff} value, suggesting that a magnetic interaction occurs among the metal ions. The overall magnetic behavior of these compounds is very similar to that for the Ru_2Cr^{III} complex reported earlier.[5] The magnetic behavior of Ru_2Co^{II} is different from that of other compounds, and the μ_{eff} vs T plot was reproducible in three independent experiments. It may be explained by considering the contribution of the orbital momentum of high-spin Co(II). In view of all the results, it appears as if M(II) behaves as an isolated ion and the two ruthenium(III) ions are effectively coupled in the trinuclear core.

The new complexes show very similar intense absorption spectra in the visible region irrespective of the type of divalent metal ion present. The absorption bands are approximately at 300, 380 (shoulder), and 550 nm for aqua complexes, and approximately at 245, 350, and 560 nm for pyridine complexes. This is in contrast to the different spectra for the Ru_2Rh^{III} and Ru_2Cr^{III} complexes.[4,5]

Cyclic voltammograms of the present new complexes show very similar three reversible one-electron redox waves irrespective of the type of divalent metal ion present. Their $E_{1/2}$'s are approximately at +0.80 to +1.11, –0.01 to +0.08, and –1.13 to –1.43 V vs Ag/Ag^+. This suggests that the redox centers are localized within the portion of "$Ru_2(\mu_3\text{-}O)$" in the mixed-metal trinuclear complexes. The three waves are assigned from the similarity of the redox potentials to diruthenium(IV,IV/III,IV), diruthenium(III,IV/III,III), and diruthenium(III,III/II,III) processes. The redox behavior of the present compounds are significantly different from those of Ru_2M^{III} (M = Rh and Cr) complexes.[4,5]

The spectroscopic and redox properties appear to represent the "$Ru_2(\mu_3\text{-}O)$" moiety. This is consistent with the conclusion from the magnetic behavior that the two ruthenium(III) ions are effectively coupled and that the divalent ion is regarded as an isolated ion. The dπ orbitals of the divalent metal ion cannot couple well with μ_3-O-pπ or Ru-dπ orbitals and do not participate well in the MO type interaction within the trinuclear core.

Very recently, two similar mixed-metal complexes $[Ru_2Co(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^{n+}$ (Co = Co(II) with $n = 0$ and Co = Co(III) with $n = 1$) were reported.[11] Their properties are not fully consistent with our observation and interpretation. Our conclusions are based on the comparison of the complexes with five different divalent metal ions and should be more general.

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Supplementary Material Available: Tables of crystallographic data, atomic positional and thermal parameters, and bond lengths and angles and labeling schemes for $[Ru_2Ni(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]\cdot py$ and $[Ru_2Co(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]\cdot py$ (8 pages). Ordering information is given on any current masthead page.

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(11) Dong, T-Y.; Lee, H-S.; Lee, T-Y.; Hsieh, C-F. *J. Chin. Chem. Soc.* **1992**, *30*, 393.